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VOL. 114

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY  
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

## AN INVESTIGATION OF THE ARBUZOV REARRANGEMENT BY THERMOGRAPHY

Academician B. A. Arbuzov and A. V. Fuzhenkova

When he discovered that phosphorous esters rearranged into alkylphosphinic esters when treated with alkyl halides, A. E. Arbuzov considered that the rearrangement proceeded via an intermediate compound formed by the addition of the alkyl halide to trivalent phosphorus. The formation of intermediate products in the case of aromatic phosphites was proved by their isolation. The case of aliphatic phosphites, the intermediate products could not be isolated, probably due to their instability.

In a previous report [3] we gave the results of investigating the reaction of phosphorous esters with alkyl halides using physico-chemical analysis - by plotting "composition-property" diagrams. In a number of cases it was shown that this method could be used for demonstrating the formation of an intermediate addition compound during the Arbuzov rearrangement.

In the present report we give the results of investigating the Arbuzov rearrangement using a thermographic method.

The thermographic method makes it easy to detect the existence of processes occurring with the evolution or absorption of heat. We therefore considered that the thermographic method would make it possible to detect the moment of formation of the intermediate compound from the addition to the trialkyl phosphite and then the moment of its decomposition into alkyl halide and alkylphosphinic ester.

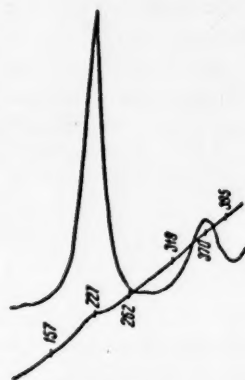


Fig. 1. Thermogram of the mixture  $P(OC_6H_5)_3$  and  $CH_3I$ . Heating rate:  $6-7^\circ/\text{min}$ .

To examine the possibilities of the thermographic method we plotted thermograms of the system triphenyl phosphite - methyl iodide, for which the addition compound had been isolated in a pure state [4], and also of some other halogen derivatives with triphenyl phosphite.

Actually, two exothermic effects were detected in the thermograms of most of the systems investigated. In some cases a third effect was detected at high temperatures, which was caused by the decomposition of the reaction product due to the high temperature.

The data for the system triphenyl phosphite - methyl iodide are given in Fig. 1. At a heating rate of  $6-7^\circ/\text{min}$  two exothermic effects at temperatures of  $227$  and  $370^\circ$  may be clearly seen on the thermogram.

Thermograms plotted for the addition compound of methyl iodide and triphenyl phosphite, which had been prepared previously, show that these two effects reflect two processes of the Arbuzov reaction. The

exothermic effect in the latter case corresponds to the second effect in the system triphenyl phosphite - methyl iodide at the same heating rate ( $3^\circ/\text{min}$ ). The second exothermic effect is observed at  $292^\circ$  for the system

\* In the literature there is also a mechanism for Arbuzov rearrangement without the participation of an intermediate product of a quasiphosphonium type [2].

triphenyl phosphite-methyl iodide, while for the addition compound, decomposition into the phenyl ester of methylphosphinic acid occurs at 293°.

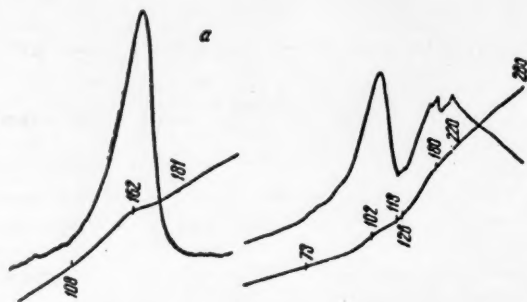


Fig. 2. Thermograms of the mixture  $P(OC_6H_5)_3$  and  $C_2H_5I$ . a) Heating rate  $5^\circ/\text{min}$ , b) heating rate  $0.4^\circ/\text{min}$ .

An equimolecular mixture of triphenyl phosphite and methyl iodide was removed from the furnace at the maximum of the first effect ( $197^\circ$ ) and cooled. The contents of the container crystallized into a solid mass of crystals of the addition compound of methyl iodide and triphenyl phosphite. On heating the container again only the second exothermic effect was obtained at  $305^\circ$ .

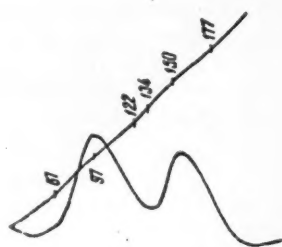
An analogous picture was obtained in the case of the system triphenyl phosphite-benzyl iodide.

Two exothermic effects were obtained on the thermograms of the systems triphenyl phosphite and methyl bromide, ethyl bromide, propyl bromide,  $\alpha$ ,  $\beta$ -dichlorodiethyl ether and  $\alpha$ ,  $\beta$ -dibromodiethyl ether, respectively.

We carried out a thermographic investigation of the reaction of aliphatic phosphites with halogen derivatives using as examples trimethyl phosphite and triethyl phosphite with the following halogen derivatives:  $CH_3I$ ,  $C_2H_5I$ ,  $iso-C_3H_7I$ ,  $iso-C_4H_9I$  and  $n-C_4H_9I$ ,  $C_6H_5CH_2I$ ,  $CH_3Br$ ,  $C_2H_5Br$ ,  $n-C_3H_7Br$ ,  $n-C_4H_9Br$ , and  $C_6H_5CH_2Br$ .

These examples showed that the reaction of the given halogen derivatives with trimethyl phosphite and triethyl phosphite at a heating rate of  $4-5^\circ/\text{min}$  is accompanied, as a rule, by only one exothermic effect. The system triethyl phosphite-ethyl iodide is given as an example (Fig. 2, a).

Fig. 3. Thermogram of the mixture  $P(OC_2H_5)_3$  and  $C_6H_5CH_2I$ . Heating rate  $4-5^\circ/\text{min}$ .



With an increase in the molecular weight of the alkyl halide the temperature at which the components react increases. The temperature at which alkyl halides of iso-structure start reacting is higher than that for normal alkyl halides.

Two exothermic effects were obtained on the thermograms of the systems triethyl phosphite-methyl bromide and triethyl phosphite-benzyl iodide: for the latter at  $97-99^\circ$  and  $150-152^\circ$  (Fig. 3). In repeating the experiments the thermograms were well reproduced. Apparently, the first effect corresponds to the formation of the addition compound of benzyl iodide and triethyl phosphite, while the second to the decomposition of the intermediate product to ethyl iodide and the ethyl ester of benzylphosphinic acid.

Only one exothermic effect was observed with benzyl bromide or chloride and triethyl phosphite under the same heating conditions.

The existence of one exothermic effect in a series of examples may be explained by the fact that at the heating rates 4-5°/min used the reaction proceeds at such a rate that both stages are not recorded separately on the thermograms, but combine into one exothermic effect.

In this case it was to be expected that two exothermic effects would appear with slower heating.

Actually, experiment showed that at a heating rate of 0.4°/min (instead of 4°/min when the reaction was completed not in 60 min. but in 11 hrs.) two exothermic effects were shown on the thermograms of the system triethyl phosphite-ethyl iodide (see Fig. 2,b).

Triethylphosphite with benzyl bromide gave only one effect when heated rapidly but at a heating rate of 0.4°/min two exothermic effects (73 and 160°) were clearly expressed on the thermogram.

Interesting results were obtained for the systems triethyl phosphite- $\alpha,\beta$ -dichloroethyl ether and triethyl phosphite- $\alpha,\beta$ -dibromoethyl ether.

V. S. Abramov and G. Karp [5] showed that  $\alpha,\beta$ -dibromodiethyl ether reacted with phosphites even at -3° with the evolution of heat. Moreover, the small and lacrimatory action of dibromodiethyl ether disappeared and a slight change in specific weight and refractive index occurred which, according to V. S. Abramov and G. Karp, indicated the formation of an intermediate product of a type.

A thermogram of an equimolecular mixture of triethyl phosphite and  $\alpha,\beta$ -dichloroethyl ether at a heating rate of 5°/min showed two exothermic effects at 155 and 200-212°. The reaction of  $\alpha,\beta$ -dibromoethyl ether and triethyl phosphite occurs at 25°. At this temperature an intermediate compound is formed. Its decomposition starts at a temperature of 117-125° (Fig. 4). That the decomposition of the intermediate addition compound specifically occurs at this temperature is indicated by the following fact. An equimolecular mixture of triethyl phosphite and  $\alpha,\beta$ -dibromodiethyl ether was kept at room temperature for 6 days after mixing and then it was heated thermographically. Only one exothermic effect was

expressed on the thermogram which corresponded to the second exothermic effect of the thermogram plotted immediately after mixing the components.

Thus the thermographic method indicates the formation of an intermediate product during the Arbuzov rearrangement not only for aromatic phosphites, but also for aliphatic esters of phosphorous acid.

In the case of aliphatic esters of phosphorous acid the intermediate products are very unstable and readily decompose into alkyl halides and esters of alkylphosphinic acid.

V. I. Ulyanova- Lenin State University of Kazan

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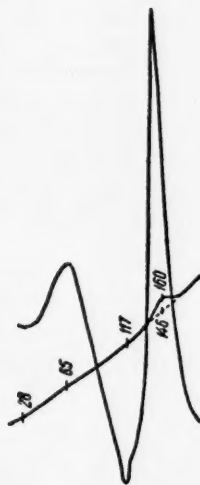


Fig. 4. Thermogram of the system  $P(OC_2H_5)_3$  and  $CH_2BrC- HBrOC_2H_5$ .

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\* Original Russian pagination. See C. B. Translation.

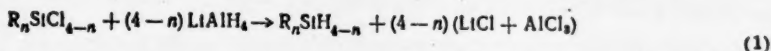


# ISOMERIC SILAPENTANES AND NEW WAYS OF SYNTHESIZING THEM

S. N. Borisov, M. G. Voronkov and B. N. Dolgov

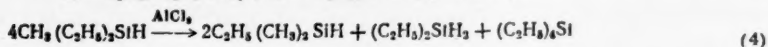
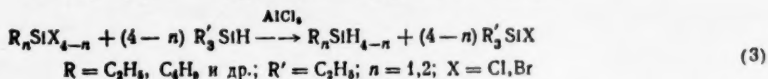
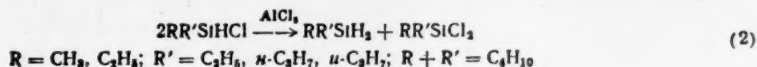
(Presented by Academician I. N. Nazarov, January 15, 1957)

Few silicohydrocarbons of the type  $R_nSiH_{4-n}$ , where R = alkyl and  $n = 1, 2$ , are known and their properties have been hardly studied. Practically the only method of preparing them is by reduction of the appropriate alkylchlorosilanes with lithium aluminum hydride [1]:



or by reaction of the appropriate silane halides  $X_nSiH_{4-n}$  with organometallic compounds [2]. Nonetheless, alkylsilanes are of considerable interest due to the specificity of their inherent chemical reactions, due to the presence of several reactive Si-H bonds, as well as to the large number of structural isomers, corresponding to one empirical formula.

To clarify the little investigated problem of the effect of the position of the silicon atom in the sillicocarbon skeleton on the properties of alkylsilanes, we synthesized a series of silapentanes  $C_4H_{12}Si$ , which could be considered as the corresponding pentanes, with a silicon substituted for one of the carbon atoms. To obtain the isomeric silapentanes new ways were developed for synthesizing them, which are expressed by the schemes:



When heated with 8-10 mole % of  $AlCl_3$ , dialkylchlorosilanes reacted 65-70% according to scheme (2) and the yield of the extremely volatile dialkylsilanes was 45-60% of the theoretical. The results of catalytic reduction of alkylsilane halides with triethylsilane (3), occurring during fractional distillation of a stoichiometric mixture of the reagents, are given in Table 1.

The data in Table 1 show that the degree of conversion of alkylsilane halides into alkylsilanes and the structure of the latter is determined both by the structure of the starting silane halide and the amount of catalyst- $AlCl_3$  (the reduction of methylpropyldichlorosilane may be accompanied by isomerization of the propyl radical).

In Table 2 are given the properties of 8 silapentanes that we prepared, as well as those of tert-butylsilane [2] and two disilapentanes-1, 2- and 1,3-disilylpropanes [3,4] in comparison with their hydrocarbon analogs—the isomeric pentanes [5].

TABLE 1

Reduction of Alkylsilane Halides with Triethylsilane

Alkylsilane halide	Amount of catalyst, mole, %	Conversion of alkylsilane halide into alkylsilane, %	Reaction product	Yield based on reacted alkylsilane halide, %
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl <sub>2</sub>	1.0	100	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiH <sub>3</sub>	52.8
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiBr <sub>2</sub>	1.5	100	The same	59.2
C <sub>2</sub> H <sub>5</sub> -n-C <sub>4</sub> H <sub>9</sub> SiCl <sub>2</sub>	1.2	36.5	CH <sub>3</sub> -n-C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub>	61.8
The same	4.0	81.3	CH <sub>3</sub> -iso-C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub> (l)	47.0
n-C <sub>4</sub> H <sub>9</sub> SiCl <sub>2</sub>	2.0	90.0	n-C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub>	98.0
iso-C <sub>4</sub> H <sub>9</sub> SiCl <sub>2</sub>	1.3	76.9	iso-C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub>	98.2
sec.-C <sub>4</sub> H <sub>9</sub> SiCl <sub>2</sub>	1.4	72.3	sec.-C <sub>4</sub> H <sub>9</sub> SiH <sub>3</sub>	97.5

TABLE 2

The Properties of Lomeric Silapentanes and Pentanes

The skeletal structure	B.p. °C (at 760 mm)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	v <sup>max</sup>	n <sub>D</sub> <sup>20</sup>	H(Si), %	
						found	calc.
C-C-C-C-C	36.1	1.3575	0.6262	115.09	0.3502	—	—
C-C-C-Si-C*	53.6	1.3857	0.6738	130.94	0.3484	2.21	2.28
C-C-C-C-Si	54.1	1.3912	0.6756	130.50	0.3518	3.23	3.43
C-C-C-Si-C*	55.6	1.3916	0.6837	129.04	0.3480	2.18	2.28
Si-C-C-C-Si	78.0	1.4235	0.7276	143.35	0.3504	—	—
C   C-C-C	27.9	1.3536	0.6196	116.20	0.3505	—	—
C   C-Si-C-C	45.7	1.3783	0.6681	132.06	0.3453	1.05	1.14
C   C-C-Si-C*	49.4	1.3790	0.6650	132.67	0.3475	2.21	2.28
C   C-C-C-Si	49.5	1.3890	0.6720	131.29	0.3510	3.05	3.43
Si   C-C-C*	49.3	1.3898	0.6738	130.94	0.3517	3.10	3.43
Si   C-C-C-Si	95(?)	—	—	—	—	—	—
C   C-C-C   C-Si-C   C-C-C	9.5	1.3513**	0.613**	117.7**	0.352**	—	—
C   C-C-C   C-Si-C   C-C-C	26.2	1.3588	0.6399	137.87	0.3430	—	—
C   C-C-C   C-Si-C   C-C-C	34.4	—	—	—	—	—	—

\* A new compound.

\*\* At 0°.

It was noted earlier [4,6] that the substitution of a carbon atom by a silicon in hydrocarbons raised the polarizability of the molecule. This, together with the greater atomic weight of silicon and greater intramolecular reaction, leads to an increase in molecular volume (by 14-16 ml/mole), boiling point (by 16-22°), specific weight (by 0.04-0.06 g/ml) and refractive index (0.02-0.04). Using silapentanes as the example, it is apparent that such a change in the physical properties is determined not only by the fact that a carbon atom is substituted by a silicon in a given hydrocarbon, but also by the position of the silicon atom in the silicocarbon skeleton, which is partially related to the number of Si-H bonds. Due to this it would hardly be worthwhile to compare the properties of silicohydrocarbons with those of hydrocarbons having similar skeletal structure. Thus, for example, of the nine isomeric silapentanes, three are analogous in structure to n-pentane, four to isopentane and two to neopentane. The development of such an analogy is, quite clearly, a formality: nonpolar tetramethylsilane, which is chemically inert due to the absence of reactive bonds at the silicon atom and polar tert-butylsilane which has three reactive Si-H bonds, are structural analogs of neopentane. It is difficult to find a common law governing the changes in physical properties from a comparison of silicohydrocarbons of similar skeletal structure as well as with alkanes structurally analogous to them. Therefore, it is more advantageous to classify silicohydrocarbons not from the point of view of their analogy to hydrocarbons, but by the electronic state of the silicon atom in them. In alkylsilanes, silicon may have four different

\*sets of bonds,\* a) 4 Si-C bonds ( $\text{SiR}_4$ ); b) 3 Si-C bonds and 1 Si-H bond ( $\text{R}_3\text{SiH}$ ); c) 2 Si-C bonds and 2 Si-H bonds ( $\text{R}_2\text{SiH}_2$ ); d) 1 Si-C bond and 3 Si-H bonds ( $\text{RSiH}_3$ ).

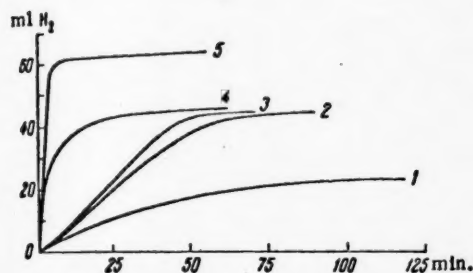


Fig. 1. The rate of hydrolysis of 0.001 mole of the isomeric silapentanes with 20% M aqueous NaOH at 750mm and 18°. 1)  $(\text{CH}_3)_2\text{C}_2\text{H}_4\text{SiH}_2$ ; 2)  $(\text{C}_2\text{H}_5)_2\text{SiH}_2$ ; 3)  $\text{CH}_3\text{n-C}_3\text{H}_7\text{SiH}_2$ ; 4)  $\text{CH}_3\text{iso-C}_3\text{H}_7\text{SiH}_2$ ; 5. n-, iso- and sec.- $\text{C}_4\text{H}_9\text{SiH}_3$ .

As was to be expected, the effect of isomerism of the radical on the rate of change of the physical constants of butylsilanes has the same character as, for example, that in the case of isomeric butyl alcohols. The structure of the radical in  $\text{C}_4\text{H}_9\text{SiH}_3$  has little effect on the lability of the Si-H bonds. (the hydrolysis rate of the three isomeric butylsilanes is almost the same). Among the isomers with the same structural skeleton, the alkylsilanes  $\text{RSiH}_3$  possess the highest values for boiling point, refractive index and refraction, while tri- and tetraalkylsilanes  $\text{R}_3\text{SiH}$  and  $\text{R}_4\text{Si}$  have the lowest. At the same time the dialkylsilanes  $\text{R}_2\text{SiH}_2$  have the greatest volatility. It is obvious in comparing the properties of silapentanes and disilapentanes that the b.p. of 1,2-disilylpropane (95°) given in the literature [3], does not correspond to the actual one  $\text{H}_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{SiH}_3$  would be expected to have a b.p. of the order of 73°.

#### EXPERIMENTAL

Synthesis of alkylsilanes by schemes (2) and (3) was carried out under the same conditions. We give the most characteristic examples.

**Diethylsilane.** 30.9 g (0.25 mole) of diethylchlorosilane was slowly distilled over 3.1 g (0.023 mole; 9.2 mole %) of  $\text{AlCl}_3$ . On redistilling the distillate, we obtained 3.8 g of diethylsilane with b.p. 54–57° (44.2%); 7.0 g of unreacted  $(\text{C}_2\text{H}_5)_2\text{SiHCl}$  (22.7% of the initial) and 12.3 g of diethyldichlorosilane with b.p. 127–129° (80.4% of theoretical on the amount of reacted diethylchlorosilane). The conversion of  $(\text{C}_2\text{H}_5)_2\text{SiHCl}$ —77.3%.

**Butylsilane.** A mixture of 26.6 g (0.14 mole) of n- $\text{C}_4\text{H}_9\text{SiCl}_3$ , 48.5 g (0.42 mole) of  $(\text{C}_2\text{H}_5)_2\text{SiH}$  and 1.5 g (0.011 mole; 2 mole %) of  $\text{AlCl}_3$  was distilled on a fractionating column to give the following fractions: I (52–56°) 10.8 g (butylsilane); II (56–143°) 2.2 g; III (143–147°) 55.7 g (Cl 25.0%, which corresponds to a mixture containing 95.2% of  $(\text{C}_2\text{H}_5)_2\text{SiCl}$  and 4.8% of  $\text{C}_4\text{H}_9\text{SiCl}_2$ ); IV (over 147°) 6.1 g. 90% of the starting n- $\text{C}_4\text{H}_9\text{SiCl}_3$  reacted. The yield of butylsilane was 98% calculated on the amount of reacted n- $\text{C}_4\text{H}_9\text{SiCl}_3$ .

**Methylisopropylsilane.** On fractionating a mixture consisting of 20.6 g (0.13 mole) of methyl-n-propyldichlorosilane, 30.6 g (0.26 mole) of triethylsilane and 2.1 g (0.016 mole; 4 mole %) of  $\text{AlCl}_3$ , we obtained 4.4 g of methylisopropylsilane with b.p. 48–52° (47%), 4.4 g of unreacted triethylsilane (14.3% of the initial), 3.9 g of unreacted  $\text{CH}_3(\text{C}_3\text{H}_7)\text{SiCl}_2$  (18.7% of the initial) and 30.1 g of triethylchlorosilane (93.5% calculated on the methyl-n-propyldichlorosilane which reacted). The conversion of  $\text{CH}_3(\text{C}_3\text{H}_7)\text{SiCl}_2$  was 81.3%. On carrying

\* The highest reactivity of methylisopropylsilane is explained by the maximum +I effect of the substituents (isopropyl group), causing polarization of the Si-H bond.

Therefore it is possible to talk of a primary etc. (up to quaternary) silicon atom in alkylsilanes. It is thus possible to group together silicon hydrocarbons with the same "set of bonds" at the Si atom but with a different structure of the silicon carbon skeleton and thus make apparent the regularity of the properties of the alkylsilanes, in relation to both the "position isomerism" of the silicon atom in the silicocarbon skeleton and the "isomerism of the hydrocarbon radical" at the silicon atom.

The rate of alkaline hydrolysis of silapentanes falls from  $\text{RSiH}_3$  to  $\text{R}_3\text{SiH}$  (Fig. 1). The specific refraction also changes in the same order ( $\text{RSiH}_3 > \text{R}_2\text{SiH}_2 > \text{R}_3\text{SiH} > \text{R}_4\text{Si}$ ). With decreasing lability of the hydrogen atom at the silicon, the silapentanes with a secondary silicon atom are arranged, in their turn, in the series:  $\text{CH}_3\text{-iso-C}_3\text{H}_7\text{SiH}_2 > \text{CH}_3\text{-n-C}_3\text{H}_7\text{SiH}_2 > (\text{C}_2\text{H}_5)_2\text{SiH}_2$ . All the physical constants (b.p.,  $d_4^{20}$ ,  $n_D^{20}$ ,  $R_D^{20}$ ) of the given dialkylsilanes also increase in exactly the same order.

out the reaction with 1 mole % of  $\text{AlCl}_3$ , the reduction proceeded normally and gave a 62% yield of methyl-n-propylsilane.

**Dimethylethylsilane.** A mixture consisting of 30.6 g (0.3 mole) of methyldiethylsilane and 1.5 g (0.0113 mole; 3.8 mole %) of  $\text{AlCl}_3$  was boiled in the flask of a distillation column for 3 hours, during which time the temperature of the reflux fell from 75 to 44°. On collecting the distillate, we obtained 9.8 g of dimethylethylsilane with b.p. 44-48° (81.2%), 4.0 g of diethylsilane with b.p. 53-58° (66.2%), 2.7 g of unreacted methyldiethylsilane (8.8% of the initial) and 7.7 g of tetraethylsilane with b.p. 149-151° ( $n_D^{20}$  1.4267;  $d_4^{20}$  0.7729; 77.9%). The conversion of methyldiethylsilane was 91.2%.

All the silapentanes investigated were colorless, mobile, volatile liquids with a sharp hydrocarbon smell, which were not spontaneously inflammable in air.

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## THE EFFECT OF SULFUR ON THE SOLUBILITY OF OXYGEN IN LIQUID IRON

Z. Buzhek and Corr. Member Acad. Sci. USSR A. Samarin

In investigating the process of desulfuration after the introduction of silicon and aluminum into an undeoxidized metal, it was established that deoxidation and desulfuration proceeded simultaneously.

In deoxidizing metal with carbon in vacuum, it was found that the final sulfur content of the metal was determined by the concentration of oxygen [1].

Considering the role that oxygen plays in desulfuration, it was necessary to establish the effect of sulfur on the solubility of oxygen in liquid iron.

The experimental effect of sulfur on the solubility of oxygen was studied by Hilty and Crafts [2], who fused the products in magnesite crucibles in a revolving furnace and an argon atmosphere. Electrolytic iron was used as the furnace charge. Pure iron sulfide and ferrous oxide were added to the molten metal. However, the results of this work are questionable. Sulfur and oxygen are metalloids, sulfur has a high solubility in liquid iron and due to this it was to be expected that the sulfur (at least in the low concentration ranges) would not have noticeable effect on the solubility of oxygen in liquid iron. The break in the solubility curves of oxygen is likewise incomprehensible.

We investigated the effect of sulfur on the solubility of oxygen in liquid iron at 1550 and 1600°. Electrolytic iron containing <0.01% C, <0.01% Mn, 0.002% S, 0.01% P and traces of Si was used as the furnace charge. The reaction between liquid iron, containing sulfur and a steam-hydrogen mixture was examined. As the smelting was carried out by the same method used for determining the oxygen activity in pure liquid iron [3] and on the same equipment, the solubility of oxygen in pure liquid iron was not determined and we limited ourselves to establishing the effect of sulfur on oxygen solubility. The ratio  $P_{H_2O} : P_{H_2}$  in the gaseous mixture was equal to one. The liquid metal was kept for 15 minutes under a mixture of this composition, which ensured the saturation of the metal with oxygen as could be seen by the appearance of a ferrous oxide on the crucible walls.

The results of the determination of oxygen solubility in liquid iron containing sulfur, at 1550 and 1600° are shown in Fig. 1.

It follows from the data obtained that sulfur, within the limits of experimental accuracy, does not affect oxygen solubility in liquid iron.

The experimental points, fixing oxygen solubility in iron-sulfur melts correspond well with the values for the maximum solubility of oxygen in pure liquid iron at 1550 and 1600°.

In other words, the relation of oxygen solubility to temperature in an iron-sulfur melt is satisfactorily expressed by the equation determining the effect of temperature on oxygen solubility in pure liquid iron [4], that is:

$$\log [\% O] = -\frac{6320}{T} + 2.734$$

The normal method of vacuum melting was used to determine the oxygen content of the metal. However, there are data [5] which show that at high concentrations of sulfur in the metal, compounds of the CS and CS<sub>2</sub> type are formed (by the reduction of oxides with carbon in vacuum) and their presence leads to higher values



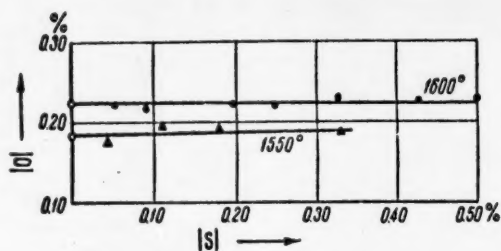


Fig. 1

in the determination of oxygen content. Therefore the results we obtained could possibly be slightly higher than those which would have been obtained if the carbon oxides had been freed from carbon sulfides.

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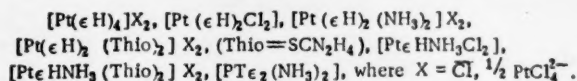
# COMPLEX COMPOUNDS OF DIVALENT PLATINUM WITH $\epsilon$ AMINOCAPROIC ACID

L. M. Volshtein and M. F. Mogilevkina

(Presented by Academician L. L. Chernyaev, September 1, 1957)

Recently we described compounds of divalent platinum ( $Pt^{2+}$ ) with  $\beta$ - and  $\gamma$ -amino acids (with  $\beta$ -alanine [1]  $\beta H$  and  $\gamma$ -amino butyric acid [2]  $\gamma H$ ). The amino group and carboxyl group in these amino acids are in the 1,3- and 1,4-positions. In the case of  $\beta H$ , an intracomplex salt (six-membered rings) was obtained, while in the case of  $\gamma H$  no intracomplex salt (it should have contained seven-membered rings) was formed. Acyclic compounds were obtained from  $\beta H$  and  $\gamma H$ . It was shown [2] that the strength of the  $Pt-AH$  bond ( $AH$ -amino acid) in acyclic compounds of the type  $[Pt(AH)_2(NH_3)_2]Cl_2$  increases in the series:  $\alpha$ -,  $\beta$ -,  $\gamma$ -amino acid.

Complex compounds with  $\epsilon$ -aminocaproic acid  $NH_2(CH_2)_5CO_2H$  (the molecules and negative ions of the acid are expressed below as  $\epsilon H$  and  $\epsilon$ -, respectively) were previously unknown. In  $\epsilon H$  the  $NH_2$  and  $CO_2H$  groups are in the 1,6-position. As was to be expected, it was impossible to obtain intracomplex salts  $[Pt \epsilon_2]$  whose rings would have been nine-membered. Only acyclic compounds were obtained.



The  $Pt-\epsilon H$  bond in compounds of the  $[Pt(\epsilon H)_2(NH_3)_2]Cl_2$  type turned out to be even more stable than that in analogous compounds with  $\gamma$ - and  $\beta$ -amino acids, and much more than in compounds with  $\alpha$ -amino acids [2]. In the case of  $\alpha$ -amino acids the only product of Jergensen splitting (by boiling with concentrate  $HCl$ ) of the compound  $[Pt(AH)_2(NH_3)_2]Cl_2$  is  $[PtCl_2(NH_3)_2]$ . In case of  $\beta H$ ,  $\gamma H$  and  $\epsilon H$  under analogous conditions a mixture of the compounds  $[Pt(AH)_2Cl_2]$  and  $[PtCl_2(NH_3)_2]$ , are formed up to  $\gamma H$  and from  $\gamma H$  to  $\epsilon H$ .

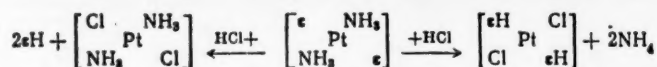
It is particularly interesting that we were able to obtain cis- and trans-isomers of the compounds  $[Pt(\epsilon H)_2Cl_2]$  and platinites with isomeric (cis- and trans-) cations  $[Pt(\epsilon H)_2(NH_3)_2]^{2+}$ . All the compounds of  $[Pt(AH)_2Cl_2]$  isolated up to the present time (9 of them are known [1-5]) have a trans-configuration. The compounds  $[Pt(AH)_2(NH_3)_2]Cl_2$  described in the literature also belong to the trans-series. Only in the case of glycine ( $GH$ ) A. A. Grinberg and B. V. Pritsyn [3] succeeded in synthesizing isomeric intracomplex salts ( $PtGl_2$ ) and in obtaining from them the salts  $[Pt(GH)_2(NH_3)_2]X_2$  with the isomeric cations (in the salt of one of the isomeric cations  $X=Cl^-$ , in the other  $X=\frac{1}{2} PtCl_4^{2-}$ ).

We shall describe briefly the preparation of some compounds with  $\epsilon H$ . By heating on a water bath a solution of  $K_2PtCl_4$  with  $\epsilon H$  and  $KOH$  (molecular ratio 1:4:4) we obtained a light yellow transparent solution. The subsequent introduction of negative ions into the inner sphere should lead to the formation of complex anions:  $[Pt\epsilon Cl_3]^{2-}$ ,  $[Pt\epsilon_2Cl_2]^{2-}$ ,  $[Pt\epsilon_3Cl]^{2-}$ ,  $[Pt\epsilon_4]^{2-}$ . It is apparent (on the basis of Chernyaev's law of the trans-effect) that the anion  $[Pt\epsilon_3Cl]^{2-}$  should have a cis-configuration. On adding hydrochloric acid to the solution obtained, the complex anions added  $H^+$  and formed:  $[Pt\epsilon HCl_3]^-$ ,  $[Pt(\epsilon H)_2Cl_2]$ ,  $[Pt(\epsilon H)_3Cl]$ ,  $[Pt(\epsilon H)_4]^{2+}$ . Moreover, the cis-dichloride  $[Pt(\epsilon H)_2Cl_2]$  and  $[Pt(\epsilon H)_4Cl_2]$ , which have low solubility in water, were precipitated. The latter compound was much more soluble in warm water than the former. After treating the mixture of  $[Pt(\epsilon H)_2Cl_2]$  and  $[Pt(\epsilon H)_4]Cl_2$  with warm water, a yellow precipitate was filtered off which turned out to be pure cis-dichloride  $[Pt(\epsilon H)_2Cl_2]$ . An acid solution of platinite was added to the cooled filtrate and a pink precipitate was formed  $[Pt(\epsilon H)_4][PtCl_4]$ .

The trans-dichloride can be formed by adding concentrated HCl to the solution obtained by reacting  $K_2PtCl_4$  with  $\epsilon$  H and KOH and then boiling the mixture, thus causing Jergensen splitting of the tetra derivative:

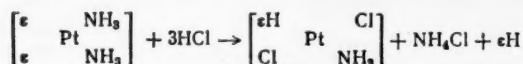


However, the precipitate that is thus formed consists of a mixture of both isomers (cis-dichloride, as already noted, is formed from the anions  $[Pt\epsilon_2Cl_2]^{2-}$ ). As both isomers have low solubility in water, it is difficult to separate them by fractional crystallization. To obtain pure trans-dichloride we used the different effect that ammonia has on the isomers. By boiling the mixture of the dichlorides with concentrated  $NH_3$  the trans-dichloride was converted into very difficultly soluble trans- $[Pt\epsilon_2(NH_3)_2]$ , and the cis-dichloride into quite soluble cis- $[Pt\epsilon_2(NH_3)_2]$ . Trans- $[Pt\epsilon_2(NH_3)_2]$  was a white precipitate, and nonelectrolyte and readily soluble in acids; with the formation of the cation  $[Pt(\epsilon H_2)(NH_3)_2]^{2+}$ . After filtering off, washing, drying and analyzing the preparation of trans- $[Pt\epsilon_2(NH_3)_2]$  was boiled in concentrated HCl. Jergensen splitting occurred according to the following scheme:



A mixture of chloride 2 of Reiset's base with trans-dichloride was precipitated; the latter product predominated (the yields were 15-20 and 40-45% respectively). The mixture was titrated with alkali; thus the acid  $[Pt(\epsilon H_2)Cl_2]$  was converted into the soluble salt  $K_2[Pt\epsilon_2Cl_2]$  (closure of the amino acid rings did not occur here, as noted above), while  $[PtCl_2(NH_3)_2]$  remained in the precipitate. Having filtered off  $[PtCl_2(NH_3)_2]$ , HCl was added to the filtrate; the acid  $[Pt(\epsilon H_2)Cl_2]$  was again obtained from the salt  $K_2[Pt\epsilon_2Cl_2]$ . The precipitate was pure trans-dichloride.

It was noted above that as a result of treatment of the dichloride mixture with  $NH_3$ , the trans- $[Pt\epsilon_2(NH_3)_2]$  precipitated while the soluble cis- $[Pt\epsilon_2(NH_3)_2]$  remained in the filtrate. Boiling the filtrate with concentrated HCl should result in Jergensen splitting:



A yellow precipitate was thus obtained; analysis showed that its composition actually corresponded to the formula  $[Pt\epsilon HNH_3Cl_2]$ ; its configuration was confirmed by treating it with Thio (the compound  $[Pt\epsilon HNH_3(Thio)_2Cl_2]$  was formed). The formation of  $[Pt\epsilon HNH_3Cl_2]$  proved the cis-structure of the soluble  $[Pt\epsilon_2(NH_3)_2]$ .

The addition of a solution of  $K_2PtCl_4$ , acidified with HCl, to the solution of cis- $[Pt\epsilon_2(NH_3)_2]$  gave a dark green precipitate of the platinite:



Trans- $[Pt\epsilon_2(NH_3)_2]$  was dissolved in dilute HCl and a solution of  $K_2PtCl_4$  was immediately added to obtain the isomeric platinite; a grey-green precipitate was formed.

The length of this article does not permit us to describe all the compounds that were prepared; we shall describe briefly the isomeric compounds.

#### Cis-dichloride

Found %: Pt 36.66; 36.82; 37.03; N 5.16

#### Trans-dichloride

Found %: Pt 36.86; 37.03; Cl 13.65; N 5.35

$[Pt(\epsilon H)_2Cl_2]$ . Calculated %: Pt 36.94; Cl 13.42; N 5.30

Platinite with a cation of cis-structure

Found %: Pt 47.09; 47.27; Cl 17.17; N 6.70; H<sup>+</sup> 0.25

Platinite with a cation of trans-structure

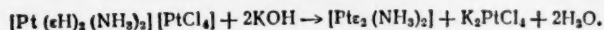
Found %: Pt 47.01; 47.17; Cl 17.48; N 6.60; H<sup>+</sup> 0.25

[Pt(εH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>][PtCl<sub>4</sub>]. Calculated %: Pt 47.12; Cl 17.12; N 6.76; H<sup>+</sup> 0.24.

The cis- and trans-dichlorides differ in shade of color (yellow and light yellow), in form, refractive index of the crystals and solubility in water (at 14° 0.00089 and 0.00025 mole/l. Both of the dichlorides are soluble in alcohol; they should be washed with water and ether and dried at 80°. When the cis-dichloride is heated with water to boiling, the solution becomes brown; the trans-dichloride solution remains yellow under the same conditions. The isomers differ sharply in their relation to Thio. By treating the isomers with thiourea under exactly the same conditions, a yellow precipitate of the tetra-thio derivative [Pt(Thio)<sub>4</sub>]Cl<sub>2</sub> was obtained from the cis-dichloride and a white precipitate of the dithio derivative [Pt(εH)<sub>2</sub>Thio<sub>2</sub>]<sub>2</sub>Cl<sub>2</sub> from the trans-dichloride. The formation of these compounds (both are obtained in a pure state and in high yields in accordance with Kurnakov's rule, confirms the configuration of the original dichlorides. Treating the cis-dichloride with NH<sub>3</sub> as noted, did not give a precipitate while the trans-dichloride gave a precipitate [Ptε<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] in > 90% yield.

The platinite with a cation of trans-configuration forms, as does Magnus' salt [Pt(NH<sub>3</sub>)<sub>4</sub>][PtCl<sub>4</sub>], two differently colored modifications. When washed with dilute HCl or water the grey-green precipitate becomes lilac; when dried it again becomes grey-green etc. The isomeric dark-green platinite does not change color when water is added. The precipitates of both isomers were washed on a filter with dilute HCl, alcohol ether and dried at 60°.

The difference in the reaction of the isomeric platinites to alkali is sharply and very graphically expressed. Both isomers were quantitatively titrated with alkali.



As they were titrated the original, colored precipitates disappeared; pink solutions of [K<sub>2</sub>PtCl<sub>4</sub>] were obtained in both cases. The platinite with the cation of cis-structure gave a transparent solution (cis-[Ptε<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] soluble) while the trans-isomer gave a white precipitate of trans-[Ptε<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]. We should note that both isomers [Pt(εH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>][PtCl<sub>4</sub>] are dimers of the monomeric compound [PtεHNH<sub>3</sub>Cl<sub>2</sub>].

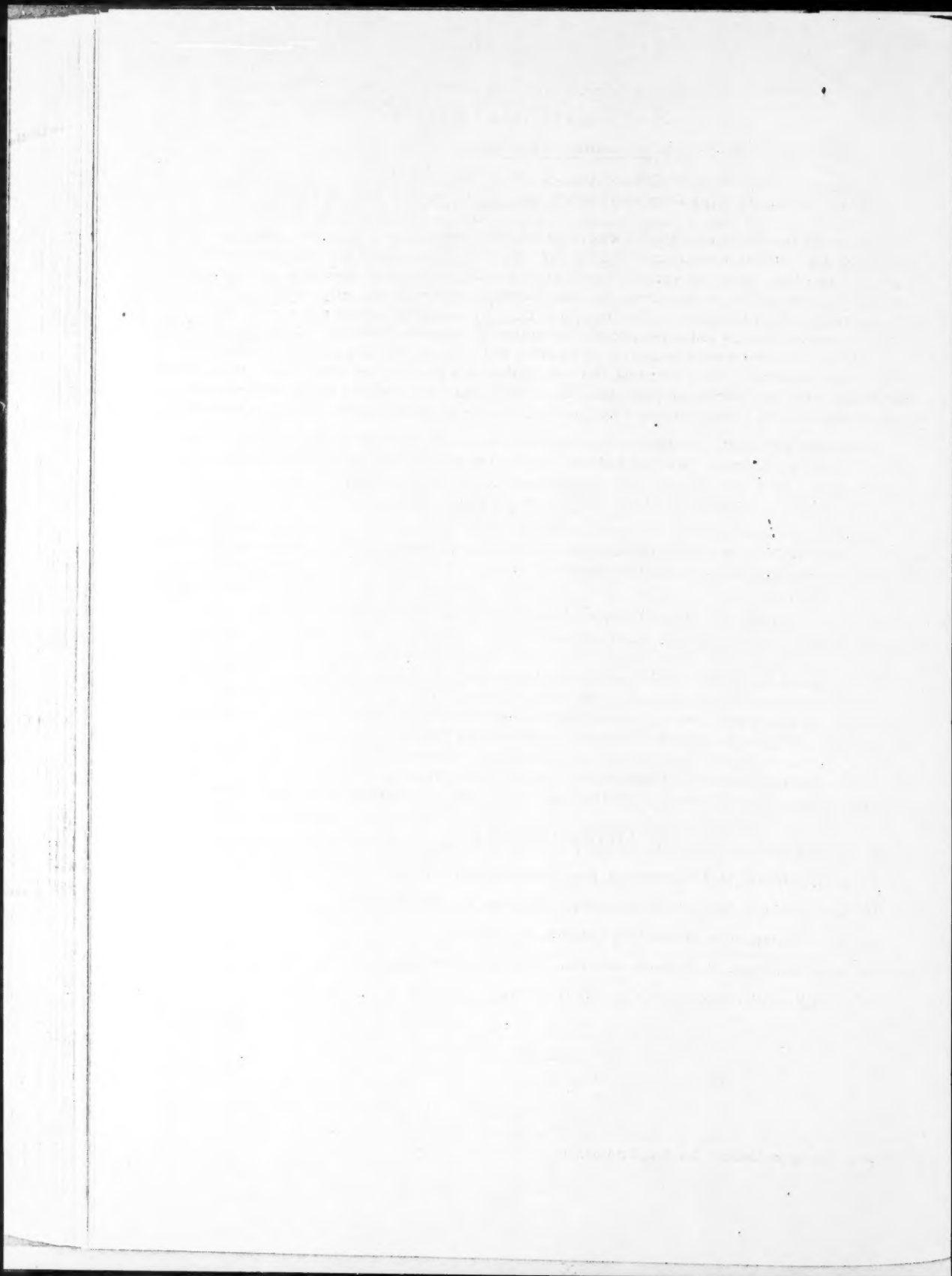
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Received December 24, 1956

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# REACTIONS OF $\beta$ -CHLORO ETHERS IN THE PRESENCE OF METALS

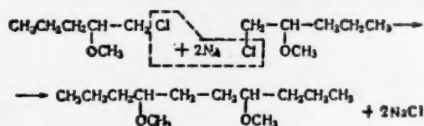
Academician of the Acad. Sci. Arm. SSR

V. I. Isagulyants and I.S. Maksimova

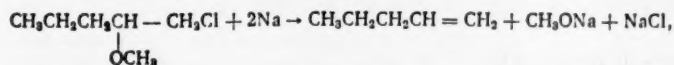
In a report [1] published earlier, a new reaction of  $\beta$ -chloro ethers was described—their capacity under certain conditions to split off hydrogen chloride with the almost quantitative formation of  $\alpha$ -substituted vinyl ethers. The new method of preparing  $\alpha$ -substituted vinyl ethers at the same time makes it possible to obtain ketones from them.

In further developing our investigations in the field of  $\beta$ -chloro ether reactions, we studied their reactions in the presence of various metals. The experiments were mainly carried out with the methyl ether of  $\alpha$ -amylen chlorohydrin and the metals: sodium, copper, aluminum and magnesium.

The following reaction was to be expected on treating the methyl ether of  $\alpha$ -amylen chlorohydrin with metallic sodium:

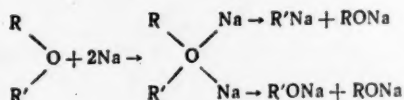


with the formation of the dimethyl ether of decanediol as the final reaction product. However, as a result of the reaction, amylen and sodium alcoholate and chloride were isolated according to the scheme:



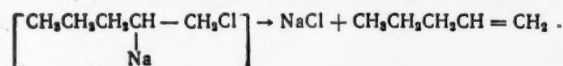
that is, there is a break in the bond  $\begin{array}{c} \text{Cl} \\ | \\ -\text{C}- \\ | \end{array}$  and  $\begin{array}{c} -\text{C}-\text{OCH}_3 \\ | \end{array}$ . According to P. P. Shorygin [2], when

ethers are treated with metallic sodium the ROF bonds break according to the scheme:



$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \begin{array}{l} \text{OCH}_3 \\ \text{CH}_2\text{Cl} \end{array} + 2\text{Na} \rightarrow \begin{array}{c} \text{CH}_3 \\ \text{O} \\ \text{Na} \end{array} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \\ \text{Na} \end{array} \begin{array}{l} \nearrow \text{CH}_3\text{ONa} + \left[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} - \text{CH}_2\text{Cl} \right] \\ \searrow \text{CH}_3\text{Na} + \left[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} - \text{CH}_2\text{Cl} \right] \end{array} \begin{array}{l} \text{Na} \\ \text{Na} \end{array} \quad \begin{array}{l} \text{(I)} \\ \text{(II)} \end{array}$$

The presence of a chlorine atom next to a sodium atom in the intermediate organo-sodium compounds results in the facile splitting off of sodium chloride and the formation of a double bond:



Under the conditions described the reaction of 43.6 g of the methyl ether of  $\alpha$ -amylene chlorohydrin with 9 g of metallic sodium gave 12 g of  $\alpha$ -amylene and 19.5 g unreacted ether. About 60% of the ether reacted.

The catalytic effect of copper on organic compounds containing a poorly labile halogen has been known for a long time (Gatterman's reaction in the case of an aromatically bound halogen). It was therefore interesting to try its effect on  $\beta$ -chloro ethers. Copper does not produce a reaction with a  $\beta$ -chloro ether. When heated to boiling with copper dust for 3 hours the  $\beta$ -chloro ether was recovered unchanged.

However, by raising the temperature to 170-300° and by carrying out the reaction under a pressure of 10 to 40 atm., HCl was split out and a substituted vinyl ether and the products of its hydrolysis and polymerization were formed. Depending on the experimental conditions, 86-96% of the original  $\beta$ -chloro ether reacted.

As a result of the experiment a gas, which contained 16 to 20% unsaturated, and a fraction with b.p. 80-120° and consisting of a mixture of vinyl ether and methyl propyl ketone, were isolated as well as high-boiling fractions which were condensation products of the substituted vinyl ether.

$$\text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OCH}_3}{\text{CH}} - \text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OCH}_3}{\text{C}} = \text{CH}_2 + \text{HCl}$$

The hydrogen chloride which separated reacted with the copper to form the chloride. The copper chloride promoted further splitting off of the hydrogen chloride,

Many samples are known where copper and its chlorides can be used as catalysts, accelerating the course of the reaction in the direction described [3-7].



The presence of copper chloride also causes the polymerization of the vinyl ether but the degree of polymerization is not great. The molecular weight of the polymers isolated, determined cryoscopically was equal to 400-470. The low degree of polymerization may be explained by the presence of a ketone in the reaction mixture: the presence of even traces of aldehydes, ketones or other oxygen-containing compounds causes a break in the polymer chains due to the formation of peroxides.

Finely divided aluminum, may be used, the same as copper, as a catalyst for splitting off hydrogen halide from organic halogen-containing compounds [8,9].

The experiments with aluminum dust were carried out in an autoclave. The temperature was varied over the range 180-280° and the pressure from 10 to 25 atm 75-91 % of the original chloro ether reacted. The reaction proceeded in the same direction as when copper was used, only with a greater yield of polymerization products in comparison with copper.

The most probable course for the reaction to take when  $\beta$ -chloro ethers were treated with magnesium appeared to be the formation of an organomagnesium compound, but actually, as in the cases where copper and aluminum were used, the reaction proceeded towards the splitting off of hydrogen chloride from the original  $\beta$ -chloro ether. A special feature of magnesium in this reaction is its capacity for catalyzing hydrolysis of the vinyl ether. The light part of the catalysate was almost pure methyl propyl ketone with a small trace of vinyl ether.

The experiments with magnesium were carried out in the temperature range of 180-280° and under a pressure of 10-30 atm. 76-80% of the original ether reacted, depending on the experimental conditions.

In comparing the effect of copper, aluminum and magnesium on a  $\beta$ -chloro ether we may conclude that the mechanism by which these metals act is the same—they all promote at first catalytic splitting out of HCl from the original ether (as described above) and then the hydrogen chloride evolved reacts with the free metal to give chlorides.

The chlorides formed further the splitting out of hydrogen chloride and catalyze secondary hydrolysis and polymerization reactions of the  $\alpha$ -substituted vinyl ether formed:

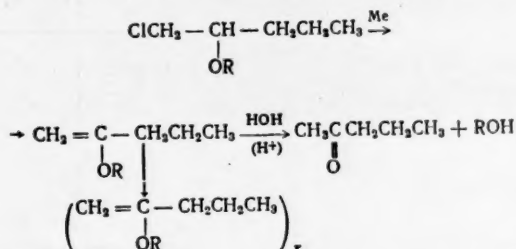


TABLE 1

The Effect of Metallic Magnesium on the Methyl ether of Amylene Chlorohydrin

Taken		Exp. conditions		Obtained						
ether, g	magnesium, g	Temp. °C	pressure atm.	gas, g	liquid amylenes, g	liquid cataly-zate, g	vinyl ether, %	Methyl propyl ketone, %	Unchanged ether, %	Conversion, %
25	6	280	25-30	2	1.8	20.8	17.1	80.05	20	80
25	6	180-200	18	1	0.8	18.6	27	72	24	76

Note:  $\alpha$ -Substituted vinyl ether and methyl propyl ketone were identified by methods described earlier [1].

TABLE 2

The Physico-chemical Properties and Analysis of  $\alpha$ -propylvinyl ether

Formula	B.p. °C	$d_4^{20}$	$n_D^{20}$	MB		MR		Bromine number	
				found	calc.	found	calc.	found	calc.
$C_5H_{10}O$	85—86	0.8043	1.4020	100.08	100	30.25	31.08	156.8	160

TABLE 3

The Physico-chemical Properties and Analysis of 2-methoxy-1-chloropentane

Formula	B.p. °C	$d_4^{20}$	$n_D^{20}$	MB		MR		C, %		H, %		Cl, %	
				found	calc.	found	calc.	found	calc.	found	calc.	found	calc.
$C_5H_{11}OCl$	140—43	0.9720	1.4290	136.15	136.5	36.54	36.28	52.42	52.79	9.44	9.52	25.9	26.40

TABLE 4

The Effect of Metallic Copper on the Methyl Ether of Amylene Chlorohydrin

Taken		Exp. conditions		Obtained						
ether, g	magnesium, g	Temp. °C	pressure atm.	gas, g	liquid amylenes, g	liquid cataly-zate, g	Vinyl ether, %	Methyl propyl ketone, %	Un-changed ether, %	Conver-sion, %
25	1	250—300	30—40	2	0.8	18.0	13.2	67.2	4	96
20	1	200—220	20—25	1.2	0.5	15.4	30.0	70	8	92
25	1	160—170	11—12	0.8	—	20.1	76	58	14	86

TABLE 5

The Effect of Metallic Aluminum on  $\alpha$ -chloro ethers (the methyl ether of amylenes chlorohydrin)

Taken		Exp. conditions		Obtained						
Alumi-num dust, g		Temp. °C	pressure atm.	gas, g	liquid amylenes, g	liquid cataly-zate, g	Vinyl ether, %	Methyl propyl ketone, %	ketone %	Conver-sion, %
20	1	280	20—25	1.8	1	17	1.5	41.65	58.3	92
25	1	200—220	10—15	0.8	—	22.4	1.6	60	39	83.6

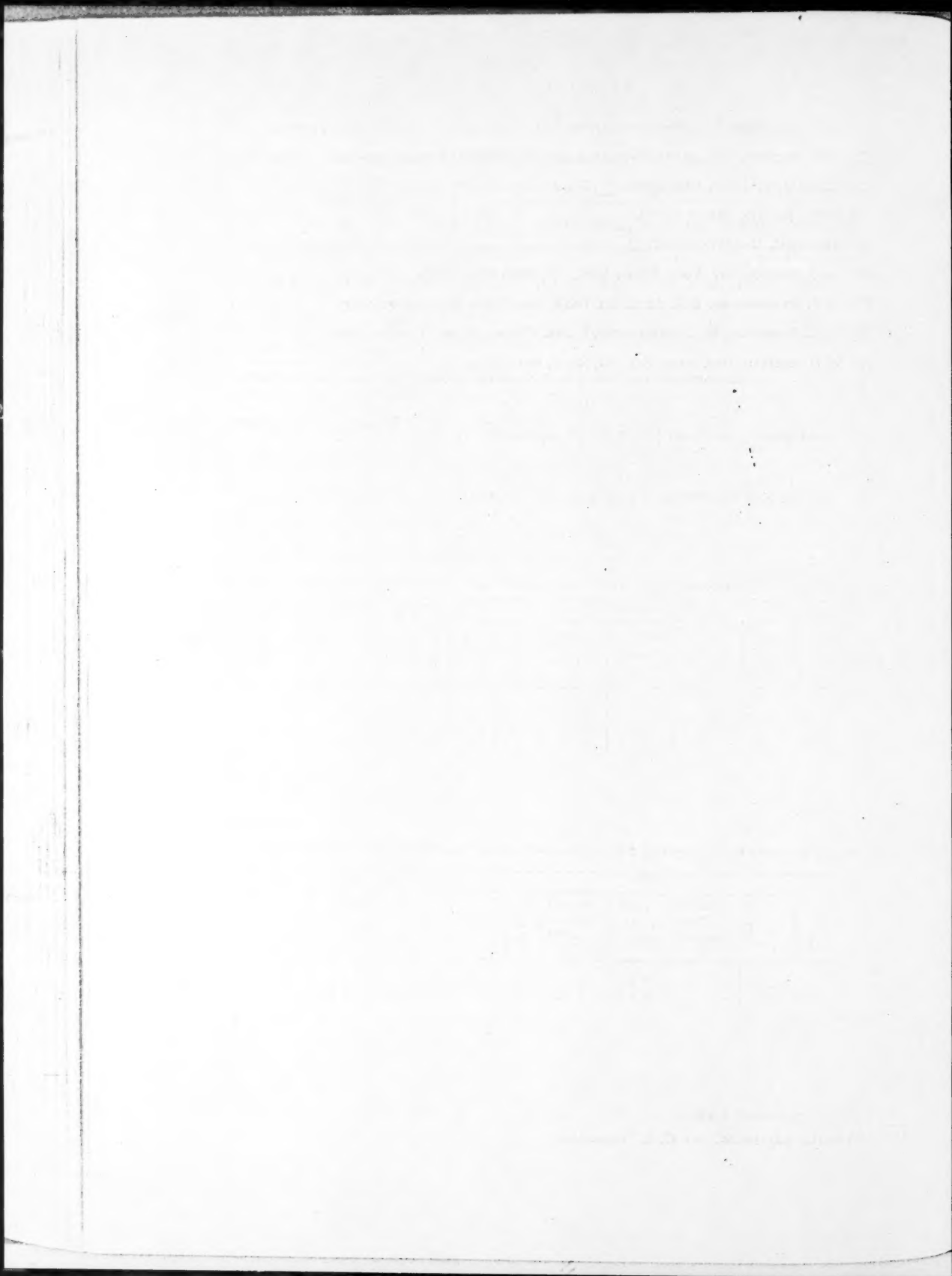
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\* Original Russian pagination. See C. B. Translation.



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## A METALLOCHEMICAL TABLE OF THE CHEMICAL ELEMENTS

I. I. Kornilov

(Presented by Academician I. P. Bardin February 1, 1957)

Recent investigations have shown the extremely important role that D. I. Mendeleev's periodic law of chemical elements has played in the development of the chemistry of metal alloys [1], or, as we now call it, metallochemistry [2], which consists of the study of the chemical reactions of metallic elements with each other or with metalloids in cases where the latter form solutions and compounds with a bond of a metallic character.

Metal reactions, from the general point of view, are characterized by the formation of two classes of complex materials—metallic solutions and metallic compounds. A peculiarity of metals is their marked tendency to form solid solutions over a wide range of concentrations. Metallic compounds as a rule are not subject to the theory of valence and in most cases possess metallic properties. Compounds with metallic properties are likewise formed as a result of the reactions of metals with certain metalloids, such as, for example, boron, carbon, silicon, nitrogen etc. These compounds have as great a tendency as metals to form solid solutions with each other or with metals.

The characteristics of the chemical reactions of metals with elements of the periodic system provide a basis for selecting a special table of the chemical elements, which would make it possible to classify solid solutions and metal compounds and to trace the gradual change from metallic compounds to compounds of metals of the ionic type. We have called this table a metallochemical table of the chemical elements in analogy with the geochemical table of the elements proposed by A. E. Fersman [3] and other authors [4].

In the geochemical table of the elements, groups are selected which are jointly or separately found in the natural state of the elements, i. e., the natural position of the elements in nature is fixed. The metallochemical table of the elements combines the elements of the Mendeleev system, which are similar and distinct in their properties, into a family for the synthesis of various types of metallic formations, starting from solid solutions and metallic compounds and ending with compounds of constant composition with an ionic type of bond.

Such a metallochemical table of the chemical elements is given in Fig. 1 and shows families of metals capable of forming: 1) continuous solid solutions, 2) limited solid solutions with metallic compounds, 3) metallic compounds without solid solutions, 4) compounds of an ionic type and 5) a group of elements incapable of reacting with the family of metals found in the middle section of the periodic system.

It can be seen from the table that the character of reaction is determined by the relative position of the metal elements in the periodic system and consequently by their electronic structure as well as by their atomic and ionic radii. The latter, as is known, change uniformly from element to element in groups and periods.

On the basis of an analysis of the families of metals arranged in the metallochemical table, it may be said that the formation of solid solutions is most characteristic of metals found in the middle section of the expanded Mendeleev table and particularly of elements in the transition groups with an incomplete d-electron shell. They are similar in chemical properties and their atomic radii differ little.

Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIIIa			1b	IIb	IIIb	IVb	Vb	VIb	VIIb
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Fr	Ra	Ac	Th	Pa	U**											

\* - lanthanides  
\*\* - actinides

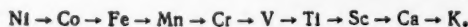


Fig. 1. A metallochemical table of the chemical elements: a) metals which form continuous solid solutions, b) metals which form limited solid solutions and metallic compounds; c) metalloids which form limited solid solutions; d) metalloids which form ionic compounds; e) metals which are incapable of reacting with metals in the middle section of the periodic system of elements.

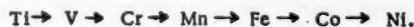
For example, the family of metals which form continuous solid solutions consists of metals of the same groups of the periodic system. This is shown by the reactions of the metals of such groups as the IV (Ti-Zr-Hf), V (V-Nb-Ta) and VI (Cr-Mo-W) groups, and of a number of metals of the VII and VIII groups, with the exception of metals with a nonisomorphic crystal structure, for example Mn and Re, Fe and Ru etc.

The tendency to form continuous solid solutions by groups similar in electronic structure, atomic radii and structural isomorphism is also found in the case of reactions of element-analogs with metallic or even metalloid properties. Thus, for example, the formation of continuous solid solutions in the group of alkali metals occurs between the analogs: potassium and cesium, cesium and rubidium; the same kind of continuous solid solutions are formed in the systems: germanium-silicon, arsenic-antimony and antimony-bismuth.

The tendency to form solid solutions in the family of these metals in the periods decreases in going from the metal-analogs to metals with different properties, or in successively going from one group to another. This corresponds to the change in their chemical properties. Thus, the tendency to form solid solutions decreases from right to left for metals of the VIII group and from left to right for metals of the IV group. For example, this decrease in solubility is expressed for Ni by the following series:



Nickel forms continuous solid solutions in this series of elements up to manganese, from chromium to Ti it forms only limited solutions, while it does not react at all from Ca to K. The reverse is observed for titanium, a metal of the IV group. The solubility of elements in titanium decreases according to the following series:



At high temperatures, titanium forms continuous solid solutions with vanadium and chromium and only limited ones with Mn, Fe, Co and Ni. Moreover, the saturated concentration of the metals with limited solubility in



titanium also decreases successively from Mn to Ni, i.e., the further the metals are from titanium [5].

The formation of metallic compounds with limited solubility and their gradual change into compounds with an ionic bond and without solid solutions happens in the family of metals in different groups quite distant from each other [6]. The formation of such compounds is particularly characteristic of reactions of metals of the main and subsidiary groups of subgroups A and B of the periodic system (see Fig. 1).

For example, it is known that magnesium is capable of giving solid solutions with those elements that are close to it in the periodic system (Cu, Ag, Au, Cd etc.) as well as with typically metallic compounds. The further the elements are from the magnesium group, the lower their capacity for forming solid solutions with magnesium, but their tendency to form compounds with a valence ratio of the atoms;  $Mg_2Si$ ,  $Mg_2Ge$ ,  $Mg_3Bi_2$  etc. increases.

Very characteristically, the group of elements belonging to the semimetals (Ge, As, Sb etc.) is characterized by a very small capacity to form solid solutions with the typical metals, among them magnesium, but these elements have a marked tendency to form compounds of the semiconductor type. Among such compounds are  $Mg_3As_2$ ,  $Mg_3Sb_2$ ,  $NiAs$ ,  $CoAs$ ,  $CoSb$ ,  $InSb$  etc.

The elements belonging to the metalloid series should be divided into two groups, one of which would consist of the group of metalloids with small atomic radii (boron, carbon, nitrogen, hydrogen and partially oxygen). This group is capable of forming limited solid solutions of the interstitial type with metals of the main groups, as well as compounds with bonds of a metallic character that gradually change from a metallic to an ionic bond.

Such compounds as borides, carbides and nitrides are typical metal compounds while oxide compounds are either semiconducting or ionic.

The metalloids, silicon and phosphorus, which have atomic radii similar to those of the metals in the main group, also belong to the group of elements that form limited solid solutions and metallic compounds of the silicide and phosphide types with these metals.

The second group of metalloids of the VI and VII groups (sulfur and halogens) belongs to the family of elements incapable of giving solid solutions with metals, but which have a marked tendency to form compounds of a typically ionic type. Moreover, characteristically, the compounds of the  $Me_xR_y$  type which are closest to metals possess to some degree inherent metallic properties (for example  $NiS$ ), the compounds which are richer in sulfur (for example  $NiS_2$ ) have semiconducting properties while the halogen metal compounds are typically ionic.

Of the metallic elements, the metals of the alkali and alkali-earth groups are in a special position in their reactions with metals. With the exception of lithium, beryllium and magnesium, they have the largest atomic radii which differ considerably from the atomic radii of most of the other metals and metalloids. They form a family of metals which are incapable of forming solid solutions with many metals either by substitution of the atoms of the solvent or, even more so, by interposition into the metal lattice of the solvent.

The particular position of this group of metals is typified by the fact that they are capable of reacting only with each other and with metals of subgroup B which have high values for their atomic radii, but are incapable of reacting with metals of the first series.

The metals of this group react with elements of subsidiary groups of the periodic system to give metallic compounds as well, with a gradual change towards ionic compounds when reacting with typical metalloids.

Thus, as a result of a brief analysis, we may state that the metallochemical table allows an overall consideration of the chemical reactions of metals with each other and with metalloids. It makes it possible to determine from the position of the metals in the periodic system, and from the chemical properties resulting from this, what types of reaction any metal is capable of entering into with other elements of the periodic system.

Using this table, one can determine the possibility of the formation of solid solutions, metallic and ionic compounds for any of the metals found in a definite position in the periodic system of elements and show which metals do not react and do not form either solid solutions or compounds. The metallochemical table of elements simplifies the classification of various types of chemical reactions of metals when metal alloys of different composition and structure are formed by them.

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## THE SYNTHESIS OF ORGANOTIN COMPOUNDS THROUGH IODONIUM SALTS

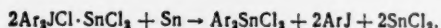
O. A. Ptitsyna, O. A. Peutov and M. F. Turchinsky

(Presented by Academician A. N. Nesmeyanov December 29, 1956)

There are few data in the literature on the use of diaryliodonium salts as starting materials for the synthesis of organometallic compounds. Thus Sandin, McClur and Irvin [1] decomposed diphenyliodonium chloride\* with mercury and tellurium in propyl alcohol and with antimony in water in the presence of  $\text{Na}_2\text{S}$  and obtained the corresponding organoelement compounds. However, the authors only give the yield of phenylmercuric chloride. L. G. Makarova and A. N. Nesmeyanov [2] used iodonium salts for the arylation of organoelement compounds. They obtained the corresponding onium organoelement compounds by the thermal decomposition of  $(\text{C}_6\text{H}_5)_2\text{I}^+\text{E}_4^-$  in the presence of materials of the  $\text{Ar}_n\text{E}$  type (where  $\text{E} = \text{Sb, As, Bi, P, Se}$ ).

We found that by decomposing the double salts of diaryliodonium chloride and heavy metal chlorides\*\* with metal powders, the corresponding organometallic compounds were formed.

In the present article we describe the synthesis of organotin compounds through double iodonium salts of stannous chloride:



It should be noted that there is no need to prepare double iodonium salts to obtain organotin compounds as we showed that diphenylstannic oxide is obtained by the decomposition of  $\text{Ar}_2\text{JCl} \cdot \text{SnCl}_2$  as well as of a mixture of  $\text{Ar}_2\text{JCl}$  and  $\text{SnCl}_2$  with tin powder. That the reaction goes through a stage of double iodonium salts in the latter case follows since, firstly, the diaryliodonium chlorides, which are poorly soluble in acetone, are dissolved by the addition of  $\text{SnCl}_2$  and, secondly  $\text{Ar}_2\text{JCl}$ , are not decomposed by tin powder under the reaction conditions and do not give organotin compounds.

The compounds synthesized by the method indicated above are given in Table 1 (the yields of organotin compounds, achieved by the Nesmeyanov diazo method [4,5] are given for comparison).

As can be seen from Table 1, the yields of organotin compounds obtained by the method of double iodonium salts are considerably greater than those achieved by Nesmeyanov's diazo method. This, together with the simplicity of the synthetic procedure makes the proposed method a convenient one for preparing aromatic organotin compounds,\*\*\*.

### EXPERIMENTAL

1. Synthesis of diphenyltin oxide. 20 g (0.063 M) of  $(\text{C}_6\text{H}_5)_2\text{JCl}$  was introduced into 25 ml of acetone and then 20 g (0.1 M) of anhydrous  $\text{SnCl}_2$  and 10 g (0.084 g atom) of powdered tin were poured in with vigorous stirring

\* Besides  $(\text{C}_6\text{H}_5)_2\text{JCl}$ , the same authors decomposed  $(\text{P-C}_6\text{H}_7)_2\text{JCl}$  with mercury and tellurium in propyl alcohol, but the yields of the corresponding organoelement compounds were not given.

\*\* The double salts of diaryliodonium chloride with  $\text{HgCl}_2$ ,  $\text{AuCl}_3$ ,  $\text{PtCl}_4$  have been known for a long time [3]. We obtained double salts with  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{SbCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{BiCl}_3$  by combining hydrochloric acid solutions of  $\text{Ar}_2\text{JCl}$  and the chlorides of the corresponding metals.

\*\*\* It should be noted that organometallic compounds of other metals ( $\text{Hg, Sb, Bi}$ ) are formed in an analogous way from double iodonium salts.

TABLE 1

Reaction products*	Yield, in %		
	through double	by Nesmeyanov's diazo method	
	iodonium salts	through double di-aryldiazonium azonium salts	through boro-fluorides*
$(C_6H_5)_2SnO$	76	23	43
$(n-C_7H_7)_2SnO$	67	—	38.4
$(n-ClC_6H_4)_2SnO$	82	4.7	21
$(n-BrC_6H_4)_2SnO$	47	6	30.2
$(n-C_6H_4)_2SnO$	39	—	—

\* All the materials obtained were identified in the form of the corresponding halides. For this purpose, a solution of the diaryltin oxide in glacial acetic acid was poured into cool, dilute hydrohalic acid; the halide precipitate formed was filtered off and recrystallized.

\*\* The total yield of organotin compounds is given.

After a while the reaction mixture heated up almost to boiling. After vigorous stirring for 4 hours the inorganic precipitate was filtered off and the solution evaporated. The oil remaining after evaporation of the acetone was washed with HCl (1:1) and dissolved in alcohol and the alcohol solution poured in the cold into a 10% solution of NaOH. The precipitate of diphenyltin oxide was filtered off and washed with water, alcohol and ether. The yield was 7 g (76% of theoretical).

Found %: Sn 41.14; 41.20; C 49.66; 49.90; H 3.79; 3.95  
 $(C_6H_5)_2SnO$ . Calculated %: Sn 41.08; C 49.87; H 3.49

**2. Synthesis of di-p-tolytin oxide.** 7 g (0.02 M) of  $(p-C_7H_7)_2ICl$  and 4 g (0.002 M) of anhydrous  $SnCl_2$  in 20 ml of acetone dissolved up 3 g (0.025 g atom) of tin. The reaction mixture was stirred for 2 hours. On working up as in the previous experiment, we isolated 2.15 g of di-p-tolytin oxide (67% of theoretical).  $(p-C_7H_7)_2SnO$  was converted into di-p-tolytin bromide. After recrystallization from petroleum ether the m.p. was 74°. Literature data [6]: m.p. 74°.

Found %: C 36.20; 36.41; H 3.05; 3.04  
 $(C_7H_7)_2SnO$ . Calculated %: C 36.49; H 3.06

**3. Synthesis of di-p-chlorophenyltin oxide.** 19 g (0.05 M) of  $(p-ClC_6H_4)_2ICl$  and 9.5 g (0.05 M) of anhydrous  $SnCl_2$  in 25 ml of acetone dissolved up 6 g (0.05 g atom) of tin. After working up, we isolated 7.25 g of di-p-chlorophenyltin oxide (82% of theoretical), which was identified as  $(p-ClC_6H_4)_2SnCl_2$ . M.p. 88°. Literature data [7]: m.p. 86.5°.

Found %: C 35.04; 35.02; H 2.07; 1.91  
 $(ClC_6H_4)_2SnCl_2$ . Calculated %: C 34.92; H 1.95

**4. Synthesis of di-p-bromophenyltin oxide.** 4 g (0.084 M) of  $(p-BrC_6H_4)_2ICl$  and 2 g (0.01 M) of anhydrous  $SnCl_2$  dissolved up 1.5 g (0.013 g atom) of powdered tin under the conditions of the previous experiment. The oil remaining after evaporating off the solvent was extracted with benzene, the benzene evaporated off and alcohol added to the residue. The alcohol solution was hydrolysed with 10% NaOH. The precipitate of di-p-bromophenyltin oxide was filtered off and washed with alcohol and ether. The yield was 1 g (47% of theoretical).  $(p-BrC_6H_4)_2SnO$  was identified as  $(p-BrC_6H_4)_2SnCl_2$ . M.p. 104°. Literature data [7]: m.p. 103°.

Found %: C 29.11; 28.91; H 1.84; 1.79  
 $(BrC_6H_4)_2SnCl_2$ . Calculated %: C 28.74; H 1.61

**5. Synthesis of di-p-iodophenyltin oxide.** 11.4 g (0.02 M) of  $(p-IC_6H_4)_2ICl$  and 4 g (0.02 M) of anhydrous  $SnCl_2$  dissolved up 3 g (0.025 g atom) of powdered tin in 20 ml of acetone. As a result of working up as in the previous experiment, we isolated 2.1 g of di-p-iodophenyltin oxide (39% of theoretical), which was identified as di-p-iodophenyltin dichloride. M.p. 147°. Literature data [7]: m.p. 147°.

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\* In this case di-p-tolytin bromide was prepared and not  $(p-C_7H_7)_2SnCl_2$ , as the latter precipitated as an oil.

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1. The first part of the paper is devoted to a general discussion of the problem of the origin of life. It is shown that the problem is one of the most important and interesting in the history of science. The author discusses the various theories of the origin of life, and shows that the most plausible is the theory of spontaneous generation. This theory is based on the fact that life is everywhere, and that it is impossible to find a place where it does not exist. The author also discusses the possibility of life existing on other planets, and shows that this is a very real possibility.

2. The second part of the paper is devoted to a discussion of the evolution of life. It is shown that life has evolved from simple to complex, and that this evolution has been the result of natural selection. The author discusses the various stages of evolution, and shows that the most important is the transition from simple to complex. This transition is the result of the fact that simple organisms are more numerous than complex ones, and that they are more likely to survive and reproduce.

3. The third part of the paper is devoted to a discussion of the future of life. It is shown that life is likely to continue to evolve, and that this evolution will be the result of natural selection. The author discusses the possibility of life existing on other planets, and shows that this is a very real possibility. The author also discusses the possibility of life existing in the form of a machine, and shows that this is a very real possibility.

4. The fourth part of the paper is devoted to a discussion of the philosophy of life. It is shown that life is a very complex and interesting phenomenon, and that it is impossible to understand it without a knowledge of the laws of nature. The author discusses the various theories of the origin of life, and shows that the most plausible is the theory of spontaneous generation. This theory is based on the fact that life is everywhere, and that it is impossible to find a place where it does not exist.

5. The fifth part of the paper is devoted to a discussion of the history of life. It is shown that life has evolved from simple to complex, and that this evolution has been the result of natural selection. The author discusses the various stages of evolution, and shows that the most important is the transition from simple to complex. This transition is the result of the fact that simple organisms are more numerous than complex ones, and that they are more likely to survive and reproduce.

6. The sixth part of the paper is devoted to a discussion of the future of life. It is shown that life is likely to continue to evolve, and that this evolution will be the result of natural selection. The author discusses the possibility of life existing on other planets, and shows that this is a very real possibility. The author also discusses the possibility of life existing in the form of a machine, and shows that this is a very real possibility.

7. The seventh part of the paper is devoted to a discussion of the philosophy of life. It is shown that life is a very complex and interesting phenomenon, and that it is impossible to understand it without a knowledge of the laws of nature. The author discusses the various theories of the origin of life, and shows that the most plausible is the theory of spontaneous generation. This theory is based on the fact that life is everywhere, and that it is impossible to find a place where it does not exist.

8. The eighth part of the paper is devoted to a discussion of the history of life. It is shown that life has evolved from simple to complex, and that this evolution has been the result of natural selection. The author discusses the various stages of evolution, and shows that the most important is the transition from simple to complex. This transition is the result of the fact that simple organisms are more numerous than complex ones, and that they are more likely to survive and reproduce.

9. The ninth part of the paper is devoted to a discussion of the future of life. It is shown that life is likely to continue to evolve, and that this evolution will be the result of natural selection. The author discusses the possibility of life existing on other planets, and shows that this is a very real possibility. The author also discusses the possibility of life existing in the form of a machine, and shows that this is a very real possibility.

10. The tenth part of the paper is devoted to a discussion of the philosophy of life. It is shown that life is a very complex and interesting phenomenon, and that it is impossible to understand it without a knowledge of the laws of nature. The author discusses the various theories of the origin of life, and shows that the most plausible is the theory of spontaneous generation. This theory is based on the fact that life is everywhere, and that it is impossible to find a place where it does not exist.



# THE PREPARATION OF CRYSTALLINE POLYPROPYLENE BY THE POLYMERIZATION OF PROPYLENE ON AN ORGANOMETALLIC CATALYST

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I. M. Tolchinsky and G. V. Garnishevskaya

Lately, the chemistry of polymeric compounds has been enriched by new methods of polymerization—stereospecific polymerization, which makes it possible to obtain stereoregular crystalline poly- $\alpha$ -olefins, Natta et al. [1], who discovered this method, give voluminous data in their report characterizing the structure and properties of stereoregular (named isotactic by them) polymers. However, the articles on this problem give almost no data on the conditions of synthesis of such polymers. Among the new forms of compounds, polypropylene, which has a series of valuable properties, is of great interest. In connection with this, it seemed interesting to investigate the conditions of preparation of crystalline polypropylene.

## EXPERIMENTAL

The starting propylene was prepared by dehydration (on aluminum oxide at 350°) of isopropyl alcohol and contained 99.2%  $C_3H_6$  and 0.8%  $N_2 + O_2$ ; in a series of experiments we used the propylene-propane fraction of petroleum gas, containing  $C_3H_6$  85.1%,  $O_2$  0.2%,  $N_2$  0.8%,  $CO_2$  0.2% (the remainder was  $C_2H_4$  and small traces of  $C_4H_8$  and  $i-C_4H_{10}$ ).

As a polymerization catalyst we used triethylaluminum in combination with titanium tetrachloride. The triethylaluminum was prepared by the method described earlier [2]. The polymerization was carried out both at atmospheric and at raised pressures. The apparatus for polymerization at atmospheric pressure is illustrated in Fig. 1.

Propylene from the container (1) passed through the gas meter (2) and flowmeter (3) and entered a system for purification from oxygen and other impurities. The purification system consisted of an electric furnace (4) with a copper filling, in which the temperature was kept at 350°, and three scrubbers (5, 6 and 7) filled respectively with granulated sodium hydroxide, ascarite and activated aluminum oxide; in work with the technical propylene-propane fraction, before the scrubbers were fitted an absorber was filled with 68%  $H_2SO_4$  to free the gas from traces of  $i-C_4H_8$ .

From purification the gas passed through a forecatalyst bottle (8) with a solution of triethylaluminum (or without it) into the reactor (9). The reactor was a glass vessel of 500 ml capacity fitted with a fast stirrer, a reflux condenser and a thermometer. A definite temperature was maintained in the reactor with a thermostatic jacket.

The reactor was first evacuated, flushed with nitrogen from the cylinder (12), which passed through the usual purification system (13-17), and then filled with solvent, which in this case was previously refined "rubber"-benzine\* with  $d_4^{20}$  0.7254 and a boiling range of 85-115°. With the help of special fittings (not shown in the diagram) a small amount of catalyst was loaded into the same reactor. The unreacted gas passed through a reflux condenser, a Tischenko bottle (10), filled with a high-boiling hydrocarbon, a gas meter (11) and then out into the atmosphere.

At the end of the experiment the reactor was cooled to +10° and the contents were stirred with absolute methanol to decompose the residual catalyst. The precipitate of polypropylene was filtered off and washed

\* T.N. "Rubber" - benzine - a purified grade of benzine with a low aromatic hydrocarbon content.

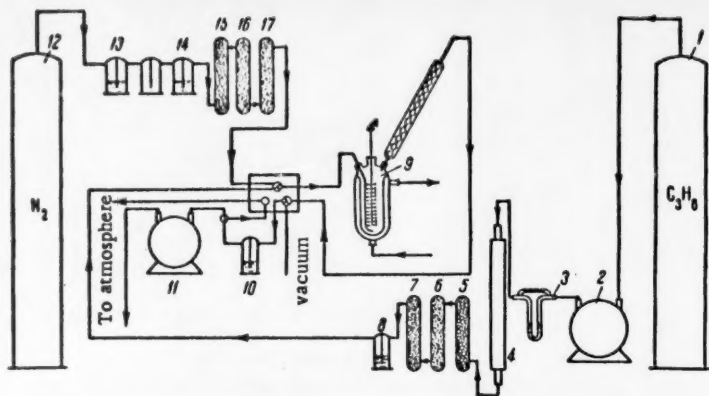


Fig. 1. Plan of apparatus for the polymerization of propylene at atmospheric pressure.

several times with methanol and water. Then the polypropylene was dried to constant weight at a temperature of 60–70° and subjected to further examination.

Experiments at slightly increased pressures (4–6 atm) were carried out in a stainless steel autoclave of 1 liter capacity, fitted with a paddle stirrer ( $n = 180$  rev/min).

Preliminary experiments showed that for polymerizations both at atmospheric and raised pressure the best results were obtained at temperatures close to 50°.

As Table 1 shows, work with pure and technical propylene gave practically the same results.

Increasing the pressure to 5–6 atm made it possible to increase the degree of conversion of the propylene significantly and to attain a polymer yield of up to approximately 150 g per liter of reaction volume in the same reaction time. The sample of polypropylene prepared at atmospheric pressure under the given conditions (Table 1) was examined in M. V. Volkenshtein's laboratory.\*

X-radiograms of the polypropylene (without examination of the texture) showed sharp rings, which are characteristic of a crystalline material. In a photomicrogram, the blackening curve did not have any obvious differences from that given by Natta. However, the "percentage of crystallinity" could not be determined by this method.

Examination of the infrared absorption spectrum of the polypropylene over a wide temperature range showed the presence of a band, characteristic of the amorphous part of the material, which increased in strength sharply on melting. The melting point practically coincided with that given by Natta. A quantitative estimate, based on the relative intensity of the "amorphous" absorption band, indicated that the given sample of polypropylene consisted of approximately 75% crystalline material.

To elucidate the effect of the molar ratio of the catalyst components on the characteristic viscosity of the polypropylene, a series of experiments was carried out in which the ratio of  $\text{Al}(\text{C}_2\text{H}_5)_3$ :  $\text{TiCl}_4$  was varied. With an increase in this ratio the characteristic viscosity (determined in decalin at 150°) increased and the melting point of the polypropylene correspondingly increased to 160–165°.

\* We would like to thank L. A. Volkova and E. I. Pokrovsky, who carried out the examination.

TABLE 1

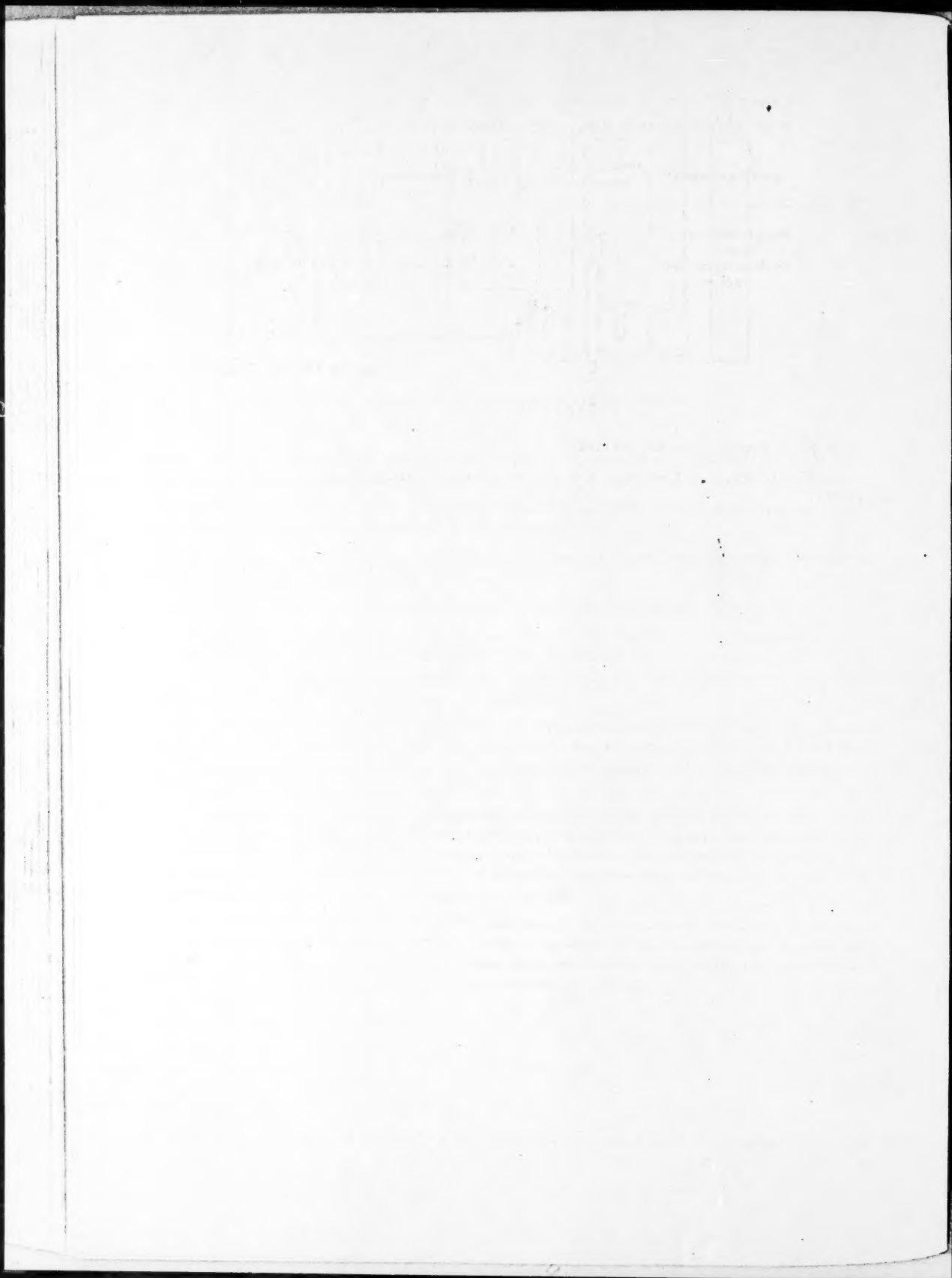
Results of Polymerization of Propylene at Atmospheric Pressure

Starting material	$\text{Al}(\text{C}_2\text{H}_5)_3$ , moles	$\text{TiCl}_4$ , moles	Con. of catalyst in sol., wt.-%	Propylene taken, liters	Unreacted propylene remaining, liters	Duration of reac- tion, hrs.	Conv. of propylene, %	Charac- teristic viscosity
Propylene from alcohol	5	1	5	70	55	3.0	21.4	0.90
Technical propylene fraction	5	1	5	68	54	3.0	20.5	0.86

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## SOME DERIVATIVES OF DIPHENYL AND THEIR TUBERCULOSTATIC ACTIVITY

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(Presented by Academician I. N. Nazarov January 15 1957)

It is known that unsubstituted aniline possesses tuberculostatic activity in vitro in concentrations of  $2 \cdot 10^{-4}$  mole/liter [1]. Para-substituted anilines, 4-aminophenol, 4-methoxyaniline, 4-ethoxyaniline and 4-propoxyaniline have a greater activity (their tuberculostatic activity appears in concentrations of  $2 \cdot 10^{-4}$ ;  $1 \cdot 10^{-4}$ ;  $1.25 \cdot 10^{-5}$ ;  $6.25 \cdot 10^{-7}$  mole/liter) [2]. 4-Aminodiphenyl turned out to be a considerably more active compound than aniline: its tuberculostatic activity appears in concentrations of  $1.25 \cdot 10^{-7}$  mole/liter [4]. Taking these observations into account, Ch. P. Ivanov and I. M. Panaiotov [5] synthesized 4-hydroxy-4-amino-diphenyl and its alkyl ethers to test them for tuberculostatic activity.

Of the derivatives of aromatic amines, azomethines and thiourea derivatives are interesting as tuberculostatic compounds. The tuberculostatic activity of azomethines was studied earlier by Erlenmeyer et al. [6] and Bauer et al. [7]. The fungicide activity of certain azomethines is also known [8]. As far as thiourea derivatives are concerned, their antitubercular and fungicide properties were the subject of several investigations [9].

During our investigations on the synthesis of compounds with possible antitubercular activity we prepared from 4-aminodiphenyl and its para-alkoxy derivatives a series of new diphenyl derivatives, namely azomethines (Table 1) and N,N'-substituted thioureas (Table 2). Besides that, we prepared azomethines which were 4-diphenyl-aldehyde derivatives.

Azomethines (Table 1) were prepared in almost quantitative yield by heating in an alcohol solution equimolecular amounts of 4-aminodiphenyl and its p-alkoxy derivatives with various aromatic aldehydes (benzaldehyde 1-5, salicylaldehyde 6-10, vanillin 11-15, para-acetylaminobenzaldehyde 16-20, cinnamaldehyde 21-25 and piperonal 26) as well as with furfural 27-31 and 9-formylacridine 32. The azomethines from 4-diphenylaldehyde were synthesized by reacting this aldehyde with aromatic amines (aniline 33, p-anisidine 34, sulfanilamide 35, 4-aminodiphenyl 36 and 4-amino-4-methoxydiphenyl 37). The azomethines obtained were yellowish or yellow crystalline materials that crystallized readily from alcohol, acetone and dioxane.

The derivatives of N-diphenyl-N'-phenylthiourea (Table 2) were obtained in good yield (80-90%) by heating in an alcohol solution equimolecular amounts of 4-aminodiphenyl and its p-alkoxy derivatives with various mustard oils (allyl mustard 1-5, p-methoxyphenyl mustard 6-10, p-ethoxyphenyl mustard 11-15 and p-chlorophenyl mustard 16-20 oils). The thioureas obtained were colorless crystalline materials that crystallized from alcohol.

The melting points and results of analysis of the azomethines are given in Table 1 and those of the thioureas in Table 2.

The azomethines—1(10), 2(11), 33(12), 36(13) (Table 1) and thiourea derivatives—6(14), 11 and 16(15) (Table 2) have been described in the literature. The other compounds given above have been prepared for the first time.

In testing the tuberculostatic activity of the azomethines in vitro in relation to the virulent  $K_1$  strain (human type) the compounds 1, 6, 11, 13, 32 (Table 1) completely stopped the growth of the bacteria in preparations with concentrations of from  $1 \cdot 10^{-6}$  to  $1 \cdot 10^{-7}$ ; the other compounds were less active or showed no tuberculostatic activity at all.

TABLE 1

No. calc.	Compound	Substit- tuents (X)	Empirical formula	M.p. °C	N, %	
					found	calc.
1		H	C <sub>15</sub> H <sub>11</sub> N	147-148 <sup>(14)</sup>		
2		HO	C <sub>15</sub> H <sub>11</sub> ON	202-203 <sup>(11)</sup>		
3		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> ON	173-174	4.90	4.88
4		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> ON	146-147	4.90	4.65
5		H	C <sub>15</sub> H <sub>11</sub> ON	180-181	4.29	4.25
6		HO	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N	140-141	5.29	5.13
7		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> N	210-212	4.85	4.84
8		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N	193-194	4.65	4.62
9		H	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N	185-186	4.64	4.41
10		HO	C <sub>15</sub> H <sub>11</sub> O <sub>3</sub> N	175-176	4.17	4.06
11		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>3</sub> N	185-186	4.82	4.62
12		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>3</sub> N	254-255	4.64	4.39
13		H	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N	186-187	4.41	4.20
14		HO	C <sub>15</sub> H <sub>11</sub> O <sub>3</sub> N	182-183	4.30	4.03
15		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>3</sub> N	129-130	4.07	3.73
16		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>3</sub> N	235-236	8.55	8.01
17		H	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N	244-246	8.66	8.84
18		HO	C <sub>15</sub> H <sub>11</sub> O <sub>3</sub> N	263-264	8.34	8.13
19		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>3</sub> N	273-279	8.06	7.82
20		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>3</sub> N	244-245	7.44	7.25
21		H	C <sub>15</sub> H <sub>11</sub> N	180-190	4.88	4.94
22		HO	C <sub>15</sub> H <sub>11</sub> ON	210-211	4.71	4.68
23		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> ON	190-191	4.63	4.47
24		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> ON	181-182	4.54	4.28
25		H	C <sub>15</sub> H <sub>11</sub> ON	175-176	4.08	3.94
26		HO	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N			
27		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> N			
28		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N			
29		H	C <sub>15</sub> H <sub>11</sub> ON	106-107	5.70	5.66
30		HO	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N	266-267	5.35	5.32
31		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> N	126-127	5.03	5.05
32		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N	157-158	4.83	4.81
33		H	C <sub>15</sub> H <sub>11</sub> ON	165-166	4.51	4.80
34		HO	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N			
35		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> N			
36		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N			
37		H	C <sub>15</sub> H <sub>11</sub> N	205-206	7.98	7.82
38		HO	C <sub>15</sub> H <sub>11</sub> ON			
39		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> ON	150-151 <sup>(15)</sup>		
40		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> ON	181-182	5.07	4.88
41		H	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> N	239-240	8.20	8.33
42		HO	C <sub>15</sub> H <sub>11</sub> O <sub>3</sub> N			
43		CH <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> O <sub>3</sub> N	245-246 <sup>(16)</sup>		
44		C <sub>6</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>15</sub> O <sub>3</sub> N	241-243	3.99	3.86

The thiourea derivatives (Table 2) did not show any activity in concentrations greater than  $1 \cdot 10^{-4}$ . Thus, the thiourea derivatives with a diphenyl residue should be regarded as compounds that are slightly active in relation to the tuberculin bacillus in vitro, though the corresponding phenyl compounds are outstanding in activity.

It is interesting that the azomethine, obtained from 4-diphenyl-aldehyde and aniline (33), has absolutely no effect on the growth of the tuberculin bacillus while the isomeric azomethine obtained from 4-aminodiphenyl and benzaldehyde (1) has a high tuberculostatic activity  $-0.2 \cdot 10^{-6}$ . Compounds 34, 35, 36 and 37 also turned out to be inactive. This indicates that the diphenyl residue has a smaller role in the appearance of antituberculosis activity than does 4-aminodiphenyl.

The toxicity of the more active azomethines 1, 6, 11 and 13 (Table 1) was tested on white mice. These azomethines turned out to be considerably less toxic than 4-aminodiphenyl, but they showed no medicinal effect in experiments on mice infected with the virulent K<sub>1</sub> strain.\*

\* Presumably, it would be interesting to test further the physiological effect of the azomethines mentioned here, in particular their carcinogenic properties, considering that 4-aminodiphenyl clearly shows carcinogenic activity [16]. It is possible that a carcinostatic material may be found among the diphenyl azomethines, especially as one of the azomethines of the fluorene series, related to the carcinogenic fluorene derivatives, displayed anticancerous activity [17].



TABLE 2

No. calc.	Compounds	Substitu- ents (X)	Empirical formula	M.p. °C	N, %	
					found	calc.
1		H	C <sub>19</sub> H <sub>19</sub> N <sub>2</sub> S	150-160	10.57	10.44
2		HO	C <sub>19</sub> H <sub>19</sub> ON <sub>2</sub> S	237-238	10.01	9.85
3		CH <sub>3</sub> O	C <sub>20</sub> H <sub>21</sub> ON <sub>2</sub> S	177-178	9.20	9.39
4		C <sub>2</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>23</sub> ON <sub>2</sub> S	169-170	8.94	8.97
5		C <sub>6</sub> H <sub>5</sub> O	C <sub>24</sub> H <sub>25</sub> ON <sub>2</sub> S	169-170	8.38	8.23
6		H	C <sub>20</sub> H <sub>21</sub> ON <sub>2</sub> S	169-170 <sup>(14)</sup>		
7		HO	C <sub>20</sub> H <sub>21</sub> O <sub>2</sub> N <sub>2</sub> S	244-246	8.33	8.00
8		CH <sub>3</sub> O	C <sub>21</sub> H <sub>23</sub> O <sub>2</sub> N <sub>2</sub> S	206-207	8.05	7.69
9		C <sub>2</sub> H <sub>5</sub> O	C <sub>22</sub> H <sub>25</sub> O <sub>2</sub> N <sub>2</sub> S	209-210	7.43	7.40
10		C <sub>6</sub> H <sub>5</sub> O	C <sub>25</sub> H <sub>27</sub> O <sub>2</sub> N <sub>2</sub> S	202-203	7.11	6.89
11		H	C <sub>21</sub> H <sub>23</sub> ON <sub>2</sub> S	197-198 <sup>(14)</sup>		
12		HO	C <sub>21</sub> H <sub>23</sub> O <sub>2</sub> N <sub>2</sub> S	243-245	7.79	7.69
13		CH <sub>3</sub> O	C <sub>22</sub> H <sub>25</sub> O <sub>2</sub> N <sub>2</sub> S	210-212	7.50	7.40
14		C <sub>2</sub> H <sub>5</sub> O	C <sub>23</sub> H <sub>27</sub> O <sub>2</sub> N <sub>2</sub> S	211-212	7.14	7.14
15		C <sub>6</sub> H <sub>5</sub> O	C <sub>26</sub> H <sub>29</sub> O <sub>2</sub> N <sub>2</sub> S	201-205	6.78	6.66
16		H	C <sub>19</sub> H <sub>19</sub> N <sub>2</sub> SCl	202-203*	8.30	8.27
17		HO	C <sub>19</sub> H <sub>19</sub> O <sub>2</sub> N <sub>2</sub> SCl	246-247	7.99	7.90
18		CH <sub>3</sub> O	C <sub>20</sub> H <sub>21</sub> O <sub>2</sub> N <sub>2</sub> SCl	215-216	7.78	7.60
19		C <sub>2</sub> H <sub>5</sub> O	C <sub>21</sub> H <sub>23</sub> O <sub>2</sub> N <sub>2</sub> SCl	216-218	7.33	7.32
20		C <sub>6</sub> H <sub>5</sub> O	C <sub>24</sub> H <sub>25</sub> O <sub>2</sub> N <sub>2</sub> SCl	205-207	6.99	6.82

\* In (15) 195°.

Microbiological testing of the compounds described here and the experiments with the white mice were carried out by the medical candidate E. I. Chertkova (Sverdlovsk Scientific Research Institute on Cancer).

## EXPERIMENTAL

**1. Preparation of 2-hydroxy-3-methoxybenzylidene-4-aminodiphenyl (11, Table 1).** To a hot solution of 1.69 g (0.01 mole) of 4-aminodiphenyl in 4 ml of alcohol was added a hot solution of 1.52 g (0.01 mole) of vanillin in 4 ml of alcohol. The mixture was heated on a water bath for half an hour. After 10 min. the solution became orange and fine crystals separated from it. On cooling, the azomethine was filtered off and dried and had m.p. 184-186°. The yield was 2.9 g (95.7% of theoretical). The product recrystallized from alcohol as yellow needles with m.p. 185-186° (for analysis see Table 1).

**2. Preparation of N-4-(4'-methoxydiphenyl)-N'-(p-ethoxydiphenyl)-thiourea (13, Table 2).** To a hot solution of 0.4 g (0.002 mole) of 4-methoxy-4-aminodiphenyl in 10 ml of alcohol was added a solution of 0.36 g (0.002 mole) of p-ethoxyphenyl mustard oil in 3 ml of alcohol. The mixture was heated on a water bath for 15 minutes and after cooling, filtering and drying, the fine colorless crystalline precipitate had m.p. 210-212°. The yield was 0.7 g (92% of theoretical). After recrystallization from alcohol it had m.p. 211-212° (for analysis see Table 2).

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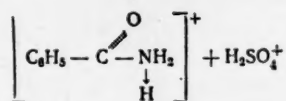
# THE STRUCTURE OF BENZOHYDROXAMIC ACIDS AND SOME OF THEIR DERIVATIVES

E. M. Usova and E. M. Voroshin

(Presented by Academician A. N. Nesmeyanov November 16, 1956)

In order to study the structural characteristics of benzhydroxamic acids and the  $\alpha$ - and  $\beta$ -forms of benzhydroxylamine in the liquid phase, we carried out an investigation on the ultraviolet absorption spectra of solutions of benzamide, mono- and dibenzhydroxamic acids and the  $\alpha$ - and  $\beta$ - forms of tribenzhydroxylamine in various solvents. The electronic spectra of solutions of these compounds were investigated by the method of quantitative ultraviolet spectrography according to Henri [1] on an ISP-22 spectrograph. The spectrum of benzamide in ethanol was the characteristic for aromatic amides with one carbonyl group (Fig. 1, 1).

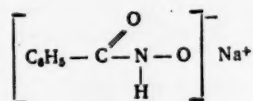
Treatment of benzamide with concentrated (96%) sulfuric acid caused the appearance of a second absorption band and increase in the intensity of the absorption maximum (see Fig. 3, 1). This can be explained by the formation of a salt due to the addition of the sulfuric acid proton to the noncovalent electron pair of the benzamide nitrogen atom:



A typical phenol absorption band (Fig. 1, 2) was detected in the spectrum of a solution of monobenzhydroxamic acid in ethanol. There was no data obtained that would indicate the existence of monobenzhydroxamic acid molecules, with a hydroxamic acid structure ( $\text{C}_6\text{H}_5 - \overset{\text{O}}{\parallel} \text{C} = \text{N} - \text{OH}$ ). Apparently, monobenzhydroxamic acid in

alcohol solution, as in the crystalline state, exists only in the form of hydroxamic acid molecules with the structure

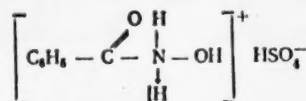
$\text{C}_6\text{H}_5 - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - \text{OH}$  [3]. The increase in intensity by 3.2 times and the displacement into the longwave region (by 40 Å) (Fig. 2, 1) of the absorption maximum of a solution of monobenzhydroxamic acid in sodium alcoholate indicates salt formation at the hydroxyl group of the monobenzhydroxamic acid:



An analogous optical effect occurs with salt formation in the phenols [2].

The absorption curve of monobenzhydroxamic acid changes similarly to the benzamide curve on treatment with sulfuric acid. A second absorption band appears in the middle ultraviolet with a maximum at  $\lambda = 2760 \text{ Å}$  and  $\epsilon = 5000$  (Fig. 3, 2). The identity of character of the changes in the spectra of monobenzhydroxamic acid and

benzamide when treated with sulfuric acid indicates similar changes in the electronic structures of these compounds. Apparently, in this case the change in spectrum is also due to the formation of a complex salt:



Dibenzohydroxamic acid in ethanol gives an electronic spectrum, analogous to the spectrum of monobenzohydroxamic acid. The difference consists of a displacement in the absorption maximum band to the ultra-violet by 60 Å and a two-fold decrease in its intensity (Fig. 1, 2, 3).

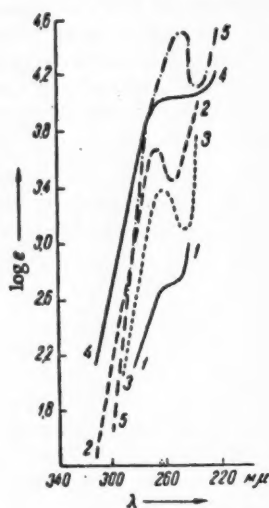


Fig. 1. Absorption spectra of solutions in alcohol ( $2 \cdot 10^{-2}$ – $2 \cdot 10^{-4}$  molar): 1. Benzamide in alcohol; 2. monobenzohydroxamic acid; 3. dibenzohydroxamic acid; 4.  $\alpha$ -form of tribenzohydroxylamine; 5.  $\beta$ -form of tribenzohydroxylamine.

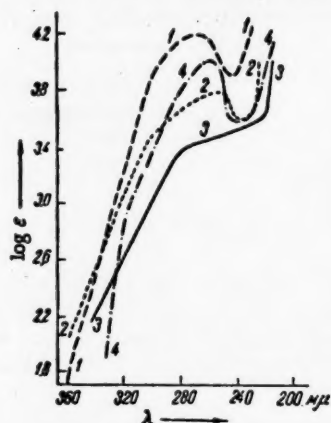
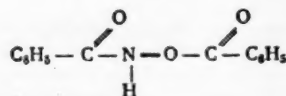
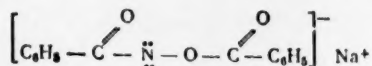


Fig. 2. Absorption spectra of solutions in sodium alcoholate ( $2 \cdot 10^{-2}$ – $2 \cdot 10^{-4}$  molar) 1. Monobenzohydroxamic acid; 2. dibenzohydroxamic acid; 3.  $\alpha$ -form of tribenzohydroxylamine; 4.  $\beta$ -form of tribenzohydroxylamine.

The similarity in the type of absorption of dibenzohydroxamic and monobenzohydroxamic acids indicates a similar chemical structure for the molecules of these materials. Therefore, a hydroxamic structure (similar to that of monobenzohydroxamic acid) may be ascribed to dibenzohydroxamic acid and the latter may be considered as the benzo ester of monobenzohydroxamic acid:



A certain displacement of the absorption maximum towards the ultraviolet and a decrease in intensity occurs due to the absence of the hydroxyl group and the presence of the ether oxygen in dibenzohydroxamic acid. The absorption band of dibenzohydroxamic acid is displaced sharply towards the long waves (by 650 Å) while the absorption maximum, on the contrary, is displaced towards the ultraviolet (by 100 Å) and increases in intensity by 1.5 times (Fig. 2,2) on sodium alcoholate treatment. This optical effect can be explained by the fact that under the effect of sodium alcoholate the formation of a salt occurs not at the hydroxyl group, as takes place in monobenzohydroxamic acid, but at the NH group due to the substitution of the H-atom by sodium:



The absorption spectrum of a solution of dibenzohydroxamic acid in concentrated sulfuric acid (Fig. 3,3) gives a basis for supposing that salt formation at the NH group is due to the addition of a sulfuric acid proton to the noncovalent electron pair of the nitrogen atom:

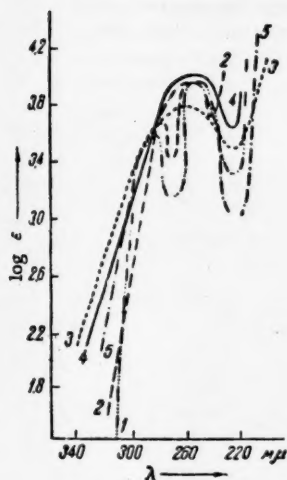
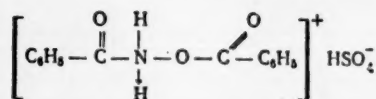


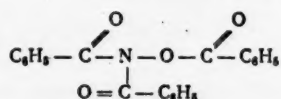
Fig. 3. The absorption spectra of solutions in 96% sulfuric acid ( $2 \cdot 10^{-2}$  -  $2 \cdot 10^{-4}$  molar): 1. Benzamide; 2. monobenzohydroxamic acid; 3. dibenzohydroxamic acid; 4.  $\alpha$ -form of tribenzohydroxylamine; 5.  $\beta$ -form of tribenzohydroxylamine.

The  $\alpha$ - and  $\beta$ -forms of tribenzohydroxylamine in solutions of ethanol and sodium alcoholate have very different spectra. This gives positive proof of the electronic structures of these materials and confirms our conclusion that the  $\alpha$ - and  $\beta$ -forms of tribenzohydroxylamine are not polymorphic modifications of the same material but are isomeric materials having different chemical structure [3].

The configuration of the absorption curve of a solution of the  $\alpha$ -form of tribenzohydroxylamine in ethanol is somewhat similar to the curve of an alcoholate solution benzamide. The curve of the  $\alpha$ -form of tribenzohydroxylamine, like that of benzamide, consists of one absorption band with a diffuse maximum, but it is distinguished by a high absorption intensity (by 20 times) (Fig. 1,4). The similarity in the benzamide and  $\alpha$ -form spectra may, most probably, be explained by considering the  $\alpha$ -form as a substituted benzamide in which two H-atoms in the  $\text{NH}_2$ -

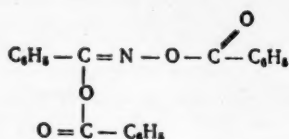
group are substituted by the benzoyl radical  $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) -$

and the ether grouping  $-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ , and the  $\alpha$ -form of tribenzohydroxylamine as having a hydroxamic structure:



Thus, it is correct to consider that the spectrum of the  $\alpha$ -form of tribenzohydroxylamine is developed from the benzamide spectrum and attains a high absorption intensity due to the effect of the reaction of the noncovalent electron pairs of nitrogen with the  $\pi$ -electrons of the carbonyl groups and noncovalent electrons

of the ether grouping. Such a conclusion agrees with those arrived at in the investigation of the infrared absorption spectra of the  $\alpha$ -form of tribenzohydroxylamine [3]. The absorption curves of the  $\beta$ -form of tribenzohydroxylamine in alcohol and sodium alcoholate have no similarities to any of the benzohydroxylamic acids' spectra and differ radically from the benzamide spectrum, which indicates that the  $\beta$ -form has a special electronic structure. The high intensity of the absorption maxima in the curves of the  $\beta$ -form in comparison with the absorption curves of the  $\alpha$ -form of tribenzohydroxylamine shows that this form is in a more excited electronic state. This hypothesis agrees with the conclusion arrived at in the investigation of the absorption spectra in the infrared region, namely, that the  $\beta$ -form has a double  $C=N$  bond, i. e. has the structure of an hydroximic acid derivative [3]:



The absorption of solutions of the  $\alpha$ - and  $\beta$ -forms of tribenzohydroxylamine in concentrated (96 %) sulfuric acid gives a somewhat different spectral picture. The differences in the spectral curves of sulfuric acid solutions of these forms disappear and their absorption maxima almost coincide (Figs. 3, 4, 5). The similarity of the absorption curves of the  $\alpha$ - and  $\beta$ -forms of tribenzohydroxylamine in the given case, apparently, can be explained by the same products which are formed by the splitting of the  $\alpha$ - and  $\beta$ -forms of tribenzohydroxylamine under treatment with sulfuric acid. Actually, as we had established experimentally, both forms of tribenzohydroxylamine are converted into dibenzohydroxamic and benzoic acids by treatment with concentrated sulfuric acid.

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# EXCHANGE OF SULFATE-IONS IN AQUEOUS SOLUTIONS OF ACIDOAMMINES OF TRIVALENT COBALT

Ya. A. Fialkov and V. D. Panasyuk

(Presented by Academician I. I. Chernyaev November 30, 1956)

The study of isotopic exchange kinetics has greatly assisted the investigation of the properties, structures and reactions of complex compounds [1,2]. The systematic investigations carried out by A. A. Grinberg et al. [1] on the mechanism and kinetics of isotopic exchange of halogen addenda in a series of complex compounds of the platinum metals are of great interest in this connection. The same type of investigations was carried out in the series of complex compounds of trivalent cobalt. The work of Ettle and Johnson [3], who investigated chlorine exchange in trans- $[\text{CoEn}_2\text{Cl}_2]^+$ , and that of Long [4] on  $\text{C}_2\text{O}_4^{2-}$  exchange in cobalt and chromium trioxalates should be noted particularly. Of later investigations in this field, those by Adamson [5], who studied the exchange of  $\text{SCN}^-$  ions in complex cobalt and chromium amines, should be mentioned.

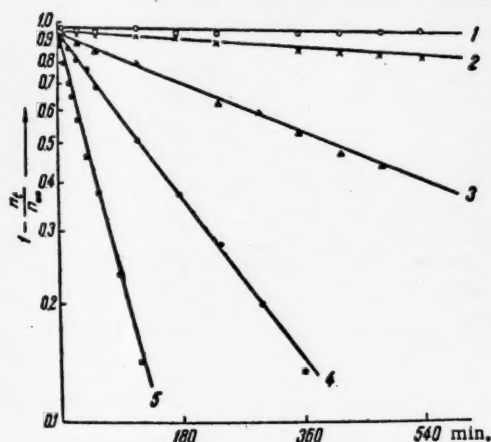


Fig. 1. The temperature relation of the rate of isotopic exchange of  $\text{SO}_4^{2-}$  ions in 0.1 N aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \cdot \text{HSO}_4 \cdot 2\text{H}_2\text{O}$ : 1) 30°, 2) 40°, 3) 50°, 4) 60°, 5) 70°.

The purpose of this work was to study the isotopic exchange of  $\text{SO}_4^{2-}$  ions in a series of acido- and acido-aquoammine salts of trivalent cobalt, containing these ions in the inner and outer coordination spheres. Isotopic exchange of sulfate ions was first examined by one of us jointly with Yu. P. Nazarenko [6] in its application to the green modifications of chromi-sulfate complexes. We investigated the exchange of sulfate ions in aqueous solutions of such cobalt acido-ammines as  $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \cdot \text{HSO}_4 \cdot 2\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4] \cdot \text{HSO}_4 \cdot 1.5\text{H}_2\text{O}$ .

In this investigation it seemed interesting to examine the lability of the  $\text{Co}^{3+} \dots \text{SO}_4^{2-}$  bond in the inner sphere, as well as the effect of inner sphere ammine and water molecules on the rate of isotopic exchange of  $\text{SO}_4^{2-}$  in aqueous solutions of these complexes.

The preparation obtained were quite pure. The amount of inner sphere sulfato-groups (the determination was carried out with benzidine hydrochloride) in both preparations equalled  $50 \pm 1\%$ .

Exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-pentammine-cobalti-bisulfate. We used  $\text{S}^{35}$  in the form of sodium sulfate as a radioactive indicator in studying the kinetics of isotopic exchange of  $\text{SO}_4^{2-}$  ions. The separation of the inner and outer sphere  $\text{SO}_4^{2-}$  ions was carried out in time, using a solution of benzidine hydrochloride. The error in separation was not greater than 1%.

The exchange rate of the ions between the outer and inner coordination spheres was studied during this work at 30, 40, 50, 60, 70° (Fig. 1). Further, the relation of the exchange rate to concentration of the complex salt (Fig. 2) and sulfate ions, found in the outer sphere (Fig. 3), was examined to establish the mechanism of the isotopic exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-pentammine-cobalti-bisulfate. The investigations of the concentration relations of the isotopic exchange rate were carried out at 60°.

The data obtained show that the exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$  proceed at a measurable rate and are described well by a kinetic equation of the first order:  $-\ln(1-F)$ .

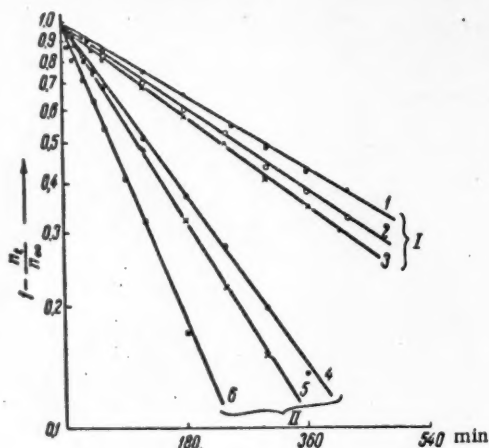
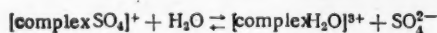


Fig. 2. The relation of the exchange rate of  $\text{SO}_4^{2-}$  ions to the concentration of complex salt in solution. I) Solutions of  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1, 5\text{H}_2\text{O}$  (40°), II) solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \cdot \text{HSO}_4 \cdot 2\text{H}_2\text{O}$  (60°), 1) 0.05 N, 2) 0.1 N, 3) 0.2 N, 4) 0.1 N, 5) 0.3 N, 6) 1 N.

The exchange rate of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-pentammine-cobalti-bisulfate changes quite rapidly with temperature. The temperature coefficient of the reaction is approximately equal to 3, the activation energy of the process of isotopic exchange is 25 Kcal/mole. The following are the values for the half-exchange times and constants of the exchange rates of  $\text{SO}_4^{2-}$  ions at various temperatures:

Temperature °C	$\tau_{1/2}$ , min	$k$ , $\text{min}^{-1}$
30	8100	$8.58 \cdot 10^{-5}$
40	2000	$3.47 \cdot 10^{-4}$
50	420	$1.65 \cdot 10^{-3}$
60	132	$5.25 \cdot 10^{-3}$
70	44	$1.58 \cdot 10^{-2}$

The process of isotopic exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4$  proceeds simultaneously with the activation of the complex ion, the increase in temperature increases the exchange rate of  $\text{SO}_4^{2-}$  ions between the outer and inner coordination spheres and the exit rate of the  $\text{SO}_4^{2-}$  ions from the inner coordination sphere increases in the same direction with the subsequent formation of an aquo ion according to the scheme:



The exchange rate of sulfate ions likewise increases with an increase in the concentration of the complex ion:

Temperature	$\tau_{1/2}$ , min	$k$ , $\text{min}^{-1}$
0.1	122	$5.25 \cdot 10^{-3}$
0.3	108	$6.42 \cdot 10^{-3}$
1.0	78	$9.12 \cdot 10^{-3}$

A ten-fold increase in the complex concentration increases the exchange rate of  $\text{SO}_4^{2-}$  ions by approximately two times (see also Fig. 2). These data give grounds for concluding that the isotopic exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ , have a bimolecular mechanism.

When investigating the effect of concentration of the outer sphere sulfate ions on the isotopic exchange rate, 5 and 10 moles of  $\text{Na}_2\text{SO}_4$  were added to each mole of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ . The results obtained (Fig. 3) indicate that the isotopic exchange rate does not depend on the concentration of the outer sphere sulfate ions. These results give grounds for concluding that there is no associative mechanism in the process of isotopic exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-pentammine-cobalti-bisulfate.

In summarizing the experimental data obtained on the relation of the isotopic exchange rate of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-pentammine-cobalti-bisulfate to temperature, time and concentration, it is possible to formulate hypothetical suppositions on the mechanism of the exchange process. The most possible hypothesis is that the process of exchange of  $\text{SO}_4^{2-}$  ions between the outer and inner coordination spheres of sulfato-pentammine-cobalti-bisulfate proceeds through the intermediate formation of the aquopentammine-cobalti-ion, i. e. the primary process is the substitution of the sulfato-group by water in the inner coordination sphere.

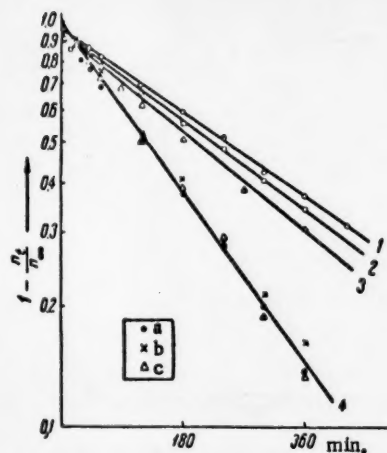
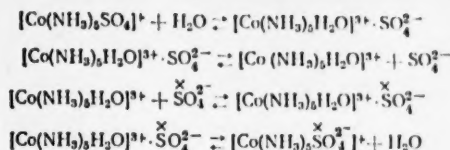


Fig. 3. The effect of sodium sulfate on the isotopic exchange rate of  $\text{SO}_4^{2-}$  ions in aqueous solutions: 1-3)  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1.5\text{H}_2\text{O}$  (40°), 1) with no additions of  $\text{Na}_2\text{SO}_4$ ; 2)  $5\text{Na}_2\text{SO}_4$  added; 3)  $10\text{Na}_2\text{SO}_4$  added; 4) aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$  (60°): a) without additions of  $\text{Na}_2\text{SO}_4$ , b)  $5\text{Na}_2\text{SO}_4$  added, c)  $10\text{Na}_2\text{SO}_4$  added.



On the basis of this mechanism for the isotopic exchange of  $\text{SO}_4^{2-}$  ions, the exchange rate should be controlled by the rate of formation of the intermediate aquo-ions (2) i.e., at higher temperatures the exchange should proceed more rapidly. This hypothesis agrees well with the experimental data obtained on the relation of exchange rate to temperature.

The exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-aquotetrammine-cobalti-bisulfate. The relation of the isotopic exchange rate of  $\text{SO}_4^{2-}$  ions to such factors as time, temperature and concentration of complex and sulfate ions in the solution was established in this work. The exchange rate of  $\text{SO}_4^{2-}$  ions in aqueous solutions of  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1.5\text{H}_2\text{O}$  sharply increases with temperature (Fig. 4). The temperature coefficient of the reaction is close to 4. The activation energy of the isotopic exchange process is 29 Kcal/mole. The values of the times of half exchange and constants of the exchange rate are given here for various temperatures:

Temperature, °C	$t_{1/2}$ , min	$k$ , $\text{min}^{-1}$
30	1260	$5.5 \cdot 10^{-4}$
40	262	$2.65 \cdot 10^{-3}$
50	68	$1.02 \cdot 10^{-2}$
60	17	$4.08 \cdot 10^{-2}$

In comparing indices, obtained during the investigation of the exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1.5\text{H}_2\text{O}$ , it can be seen that with all other conditions equal, exchange in the latter proceeds much more rapidly. The rate of isotopic exchange in aqueous solutions of aquo-tetrammine-cobalti bisulfate changes more sharply with temperature. Consequently, substitution of ammonia molecules by water in the inner coordination

sphere of a complex ion increases the lability of the complex-bound sulfato-groups.

An investigation of the exchange rate of  $\text{SO}_4^{2-}$  ions at different concentrations of the complex salts in the solution gave, generally, the same relation as in the preceding system \* (see Fig. 2):

Conc., equiv/l	$t_{1/2}$ , min	$k$ , $\text{min}^{-1}$
0.05	296	$2.34 \cdot 10^{-3}$
0.1	262	$2.65 \cdot 10^{-3}$
0.2	236	$2.94 \cdot 10^{-3}$

The results obtained in investigating the relation of the exchange rate to concentration of outer-sphere sulfate ions are shown in Fig. 3; for this purpose 5 and 10 moles of  $\text{Na}_2\text{SO}_4$  were added for each mole of  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1.5\text{H}_2\text{O}$ . A certain increase in the isotopic exchange rate was observed in aqueous solutions of this complex with an increase in the concentration of  $\text{SO}_4^{2-}$  ions.

However, this slight change in the isotopic exchange rate does not justify speaking of different exchange mechanisms in aqueous solutions of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1.5\text{H}_2\text{O}$ .

The experimental data obtained give grounds for supposing that the first stage in the isotopic exchange of  $\text{SO}_4^{2-}$  ions in aqueous solutions of sulfato-aquo-tetrammine-cobalti-bisulfate is the activation of the complex ion with the formation of the diaquo-form according to the scheme:

\* The low solubility of the complex salt made it impossible to investigate the exchange of  $\text{SO}_4^{2-}$  at  $> 0.2\text{N}$  concentrations.

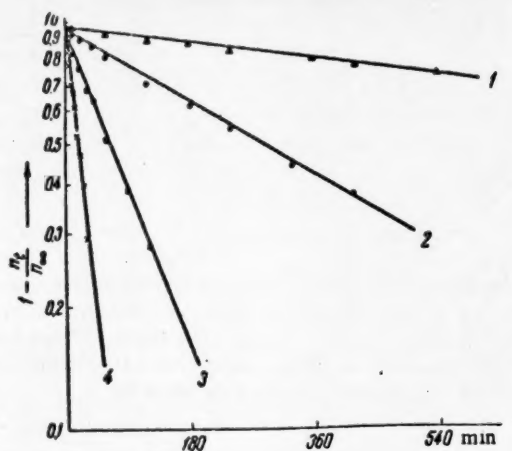
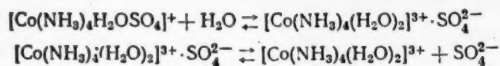


Fig. 4. Temperature variation of the rate of isotopic exchange of  $\text{SO}_4^{2-}$  ions in 0.1 N aqueous solutions of  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OSO}_4]\text{HSO}_4 \cdot 1, 5\text{H}_2\text{O}$ . 1) 30°, 2) 40°, 3) 50°, 4) 60°.



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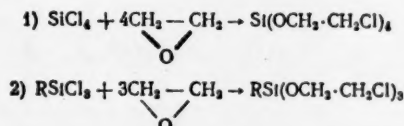
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# THE REACTION OF ETHYLENE OXIDE WITH SILICON TETRACHLORIDE AND ETHYLTRICHLOROSILANE

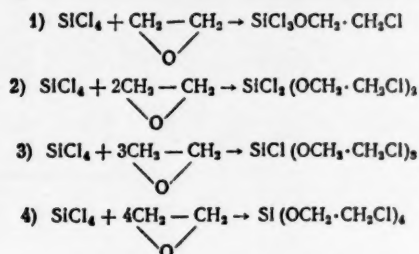
M. F. Shostakovsky and S. P. Lavrov

(Presented by Academician I. N. Nazarov January 15, 1957)

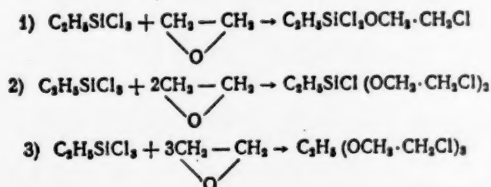
The reaction of  $\alpha$ -oxides of the ethylene series with silicon tetrachloride and alkyl (aryl) chlorosilanes is partially described in the literature [1-5]. However, the products of complete reaction of ethylene oxide with silicon tetrachloride and also with its substituted derivatives were usually obtained. As is known, the reactions proceed according to the schemes:



Meanwhile, it should be possible to obtain not only the products of complete reaction, but also a series of materials, produced as a result of partial (incomplete) reaction of silicon tetrachloride and its substituted derivatives with ethylene oxide. This may be shown by the following equations for silicon tetrachloride:



The reaction of ethyltrichlorosilane with ethylene oxide may be expressed by the equations:



We found conditions for the preparation and isolation of products of incomplete reaction of silicon tetrachloride and ethyltrichlorosilane with ethylene oxide. These products have not been described in the literature previously.

TABLE 1

Name of material	Formula	Yield of 2-chloroethoxy-chlorosilanes, %	B.p. in °C (mm Hg)	$D_{20}^{20}$	C, %		H, %		Si, %		Cl, %	
					found	calc.	found	calc.	found	calc.	found	calc.
2-Chloroethoxy-ethylchlorosilane	$C_2H_5SiCl_2OCH_2CH_2Cl$	44.13	173-174 (760)	1.2360	23.20	23.14	4.44	4.33	13.43	13.50	50.94	51.32
Di-2-chloroethoxy-ethylchlorosilane	$C_4H_{10}SiCl(OCH_2CH_2Cl)_2$	40.01	86 (3)	1.2362	23.40	28.64	4.53	5.15	13.80	11.13	50.61	42.31
Tri-2-chloroethoxy-ethylsilane	$C_6H_{16}Si(OCH_2CH_2Cl)_3$	80.00	122-123 (3)	1.2361	28.60	32.48	5.19	5.76	11.14	9.41	42.99	35.88
2-Chloroethoxy-trichlorosilane	$SiCl_3OCH_2CH_2Cl$	69.42	153-154 (760)	1.4376	28.81	32.29	5.28	5.82	11.36	9.67	36.17	36.79
Di-2-chloroethoxy-dichlorosilane	$SiCl_2(OCH_2CH_2Cl)_2$	54.58	228-227 (760)	1.4068	11.36	11.12	1.98	1.90	13.10	13.03	65.57	65.92
Tri-2-chloroethoxy-chlorosilane	$SiCl(OCH_2CH_2Cl)_3$	47.01	123 (3)	1.3738	11.41	18.86	2.02	3.05	13.14	10.82	65.62	54.98
Tetra-2-chloroethoxysilane	$Si(OCH_2CH_2Cl)_4$	81.00	159 (3)	1.3437	18.70	23.98	3.15	3.97	11.10	9.4	54.34	46.99
					24.02	28.04	4.03	4.61	9.28	8.09	46.46	41.01
					27.91	27.53	4.61	4.58	8.16	7.98	41.62	41.83



## EXPERIMENTAL

As an example of the conditions used to prepare substances by the reaction of ethylene oxide with silicon tetrachloride or with ethyltrichlorosilane, we will consider the preparation of 2-chloroethoxyethylchlorosilane.

To 32.6 g (0.2 mole) of cooled (ice) ethyltrichlorosilane with b.p. 98-99° (760 mm) and  $D_{20}^{20}$  1.2380 liquid ethylene oxide was added gradually with stirring until the weight increased by 8.8 g (0.2 mole). If the reaction did not begin immediately, the reaction vessel was taken out of the ice (the beginning of the reaction was indicated by an increase in temperature of the reaction mixture).

At the end of the reaction the reaction mixture was fractionally distilled. We isolated 15.8 g (44.13% of theoretical) of 2-chloroethoxyethylchlorosilane with b.p. 173-174° (760 mm),  $D_{20}^{20}$  1.2365.

Found %: C 23.40; H 23.20; Si 4.44; 4.53; Cl 13.43; 13.80; 50.92; 51.32  $C_4H_9SiOCl_3$ . Calculated %: C 23.14; H 4.33 Si 13.50; Cl 51.32

The rest of the products were prepared by similar methods. Some of their physico-chemical properties are given in Table 1.

The products of the incomplete reaction of ethylene oxide with silicon tetrachloride and ethyltrichlorosilane were liquids with an acrid smell, fuming in air and readily soluble in organic solvents.

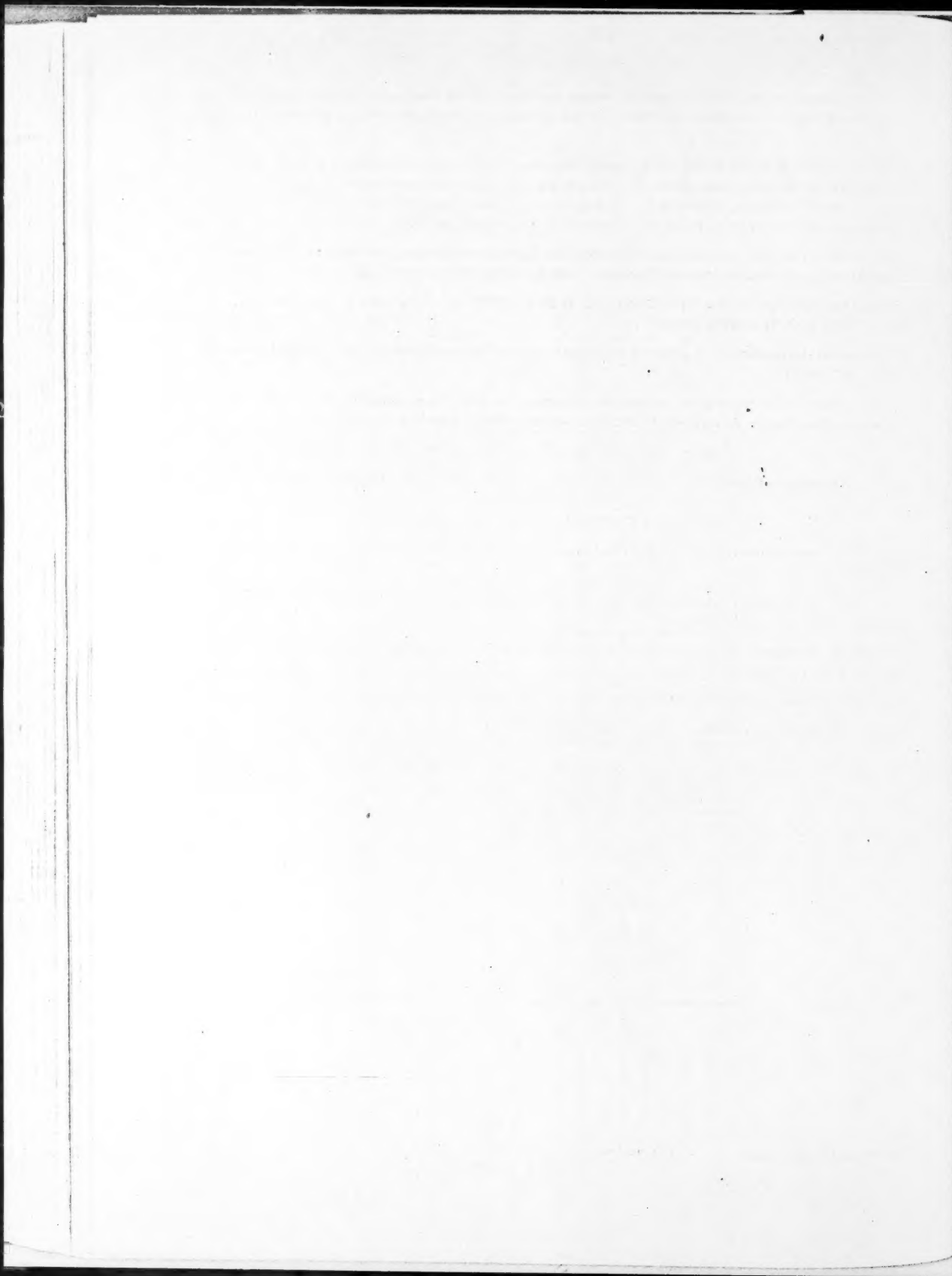
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\* Original Russian pagination. See C.B. Translation.



# ON THE RELATION BETWEEN THE CHEMICAL STRUCTURE OF CARBOCYCLIC AND HETEROCYCLIC COMPOUNDS AND THEIR SCINTILLATION ACTIVITY

N. A. Adreva, M. M. Koton, Yu. N. Panov and F. S. Florinsky

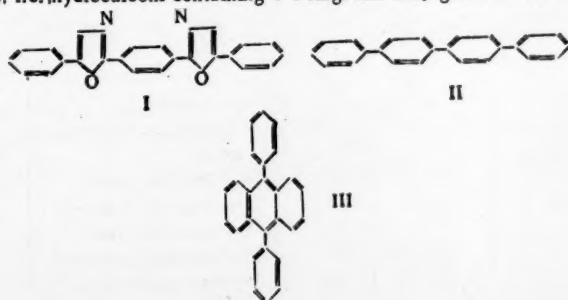
(Presented by Academician A.N. Terenin, December 12, 1956)

Organic phosphors have recently been publicized and are being widely employed in the form of crystalline, liquid and plastic scintillators. Inorganic phosphors have been known for some time.

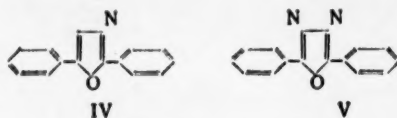
Fluorescent organic compounds include the majority of aromatic hydrocarbons and a considerable number of heterocyclic compounds whose molecules have a ring structure and contain conjugated double bonds.

A study of the relation between the chemical structure of organic compounds and their scintillating activity presents undoubted interest with the objective of establishing correlations that would permit organic scintillators to be tailor-made with the optimum luminescent properties. Many such investigations have been carried out in connection with the properties of crystalline [1] and liquid [2] scintillators; plastic scintillators [3] have not been studied so extensively although they are invested with great interest since due to certain of their properties they are destined to replace crystalline and liquid scintillators to a considerable extent.

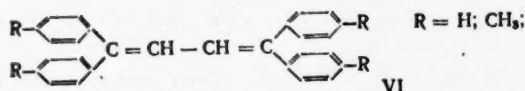
We investigated the scintillating activity of substituted anthracenes, polyphenyls, aryl derivatives of dienes and a series of heterocyclic compounds (60 compounds in all) after introducing them into a polystyrene plastic mass. The substances were incorporated into styrene monomer in amounts corresponding to their maximum intensity (1-2%) and polymerization was effected in presence of 0.2% of benzoyl peroxide by gradual raising of the temperature from 80 to 120° in the course of 4-5 days. Hard, transparent blocks were obtained and these were shaped into cylinders. The latter were investigated for their scintillating efficiency with the help of an apparatus that enabled determination of the relative magnitude of the voltage peak at the outlet of a photoelectric multiplier (FEU-19). The peak of a standard sample (2% terphenyl in polystyrene) was taken as 100% at a counter level of 1000 pulses/min. By maintaining a constant counter level for all the substances investigated by altering the cutoff voltage at the outlet of the discriminator, we can obtain the cutoff voltage of each sample. Comparative data for evaluation of the samples are obtained by comparing these values with the cutoff voltage of the standard. The peak value of the standard is 50% of the peak value of a stilbene crystal. The investigation indicated the existence of a relation between the chemical structure of organic compounds and their scintillating efficiency. Table 1 shows that the highest efficiency when incorporated in a plastic mass is exhibited by 1,4-di-(2-(5-phenyloxazolyl)-benzene)(I) (POPOP), quaterphenyl (II) and 9,10-diphenylanthracene (III), i.e., hydrocarbons containing 4-5 rings and conjugated double bonds.



In a series of intensely scintillating oxazoles and oxadiazoles the scintillating efficiency depends in very great measure on the nature of the substituents in the 2,5-position. For a given substituent (phenyl) the oxazoles (IV) have a higher scintillating efficiency than derivatives of oxadiazoles (V)



These data are in good agreement with those of Hayes and others [4] which were obtained in a study of liquid scintillators. High scintillating efficiency is likewise exhibited by 1,1,4,4-tetraarylbutadienes (VI)



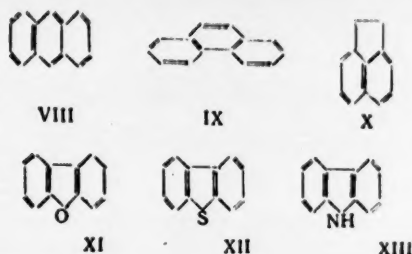
and by p-terphenyl (VII)



A correlation of chemical structure and scintillating efficiency is also found for the group of hydrocarbons with three condensed nuclei and differing from one another in ring structure, number of conjugations and the presence of different heterocycles (O, S, NH). Anthracene (VIII) is more efficient than phenanthrene (IX) and acenaphthene (X), while in the series of dibenzo derivatives of furan (XI), thiophene (XII) and pyrrole (XIII), the highest scintillating efficiency is exhibited by the oxygen-containing heterocycle (XI).

TABLE 1

Organic Compound	Concentration in polystyrene (weight-%)	Relative magnitude of impulses (%)	Organic Compound	Concentration in polystyrene (weight-%)	Relative magnitude of impulses (%)
1,4-Di-(2-(5-phenyloxazolyl)-benzene) (POPOP)	0.5	105	Dibenzopyrrole	2.0	(2)
Quaterphenyl	0.5	95	Ditolylmethane	2.0	10
9,10-Diphenylanthracene	0.5	80-85	Dixylylmethane	2.0	9
2,5-Diphenyloxazole	1.0	105-115	Dinaphthylmethane	2.0	31
2-( $\alpha$ -Naphthyl)-5-phenyloxazole ( $\alpha$ -NPO)	1.0	105	9,10-Di-(p-methoxyphenyl)-anthracene	2.0	96
2-( $\omega$ -Styryl)-5-phenyloxazole	1.0	67	9,10-Di-m-tolyl-anthracene	2.0	77
2,5-Diphenyloxadiazole	1.0	75	9,10-Di-(p-tolyl)-anthracene	2.0	72
1,1,4,4-Tetraphenylbutadiene	1.0	75-85	9,10-Di-(p-bromophenyl)-anthracene	2.0	72
1,1,4,4-Tetratolylbutadiene	1.0	70-75	9,10-Di-acetoaminoanthracene	2.0	38
p-Terphenyl	2.0	100	9-n-Butylanthracene	2.0	52
Anthracene	2.0	30	9-n-Propylanthracene	2.0	46
Phenanthrene	2.0	15	9-Ethylanthracene	2.0	44
Acenaphthene	2.0	10	9-Methylanthracene	2.0	30
Dibenzofuran	2.0	15	2-Methylanthracene	2.0	35
Dibenzothiophene	2.0	5			

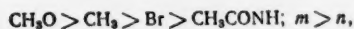


These results, obtained in a study of plastic compositions, are consistent with the data of Sangster [1], obtained in a study of the scintillating efficiency of the same substances in the crystalline state. Low efficiency is exhibited by the various diarylmethanes (XIV) in whose molecules the conjugation between the benzene rings is upset:



Only after increase of the number of rings to four in such a molecule, as happens in dinaphthylmethane, does the scintillating efficiency rise from 9% to 31%. Diphenylmethane also has a low efficiency in the crystalline state [2].

It must be noted that with introduction of substituents into the benzene ring of a hydrocarbon their chemical character as well as their isomerism has an appreciable influence upon the scintillating efficiency. We observed this in the case of 9-substituted anthracenes:



while Hayes [4] observed it in the case of derivatives of oxazoles and oxadiazoles. Also of interest is the rise in scintillating activity of 9-substituted anthracenes on passing from the methyl to the butyl radical.

The authors thank A.S. Cherkasov for kindly placing a series of substituted anthracenes at their disposal.

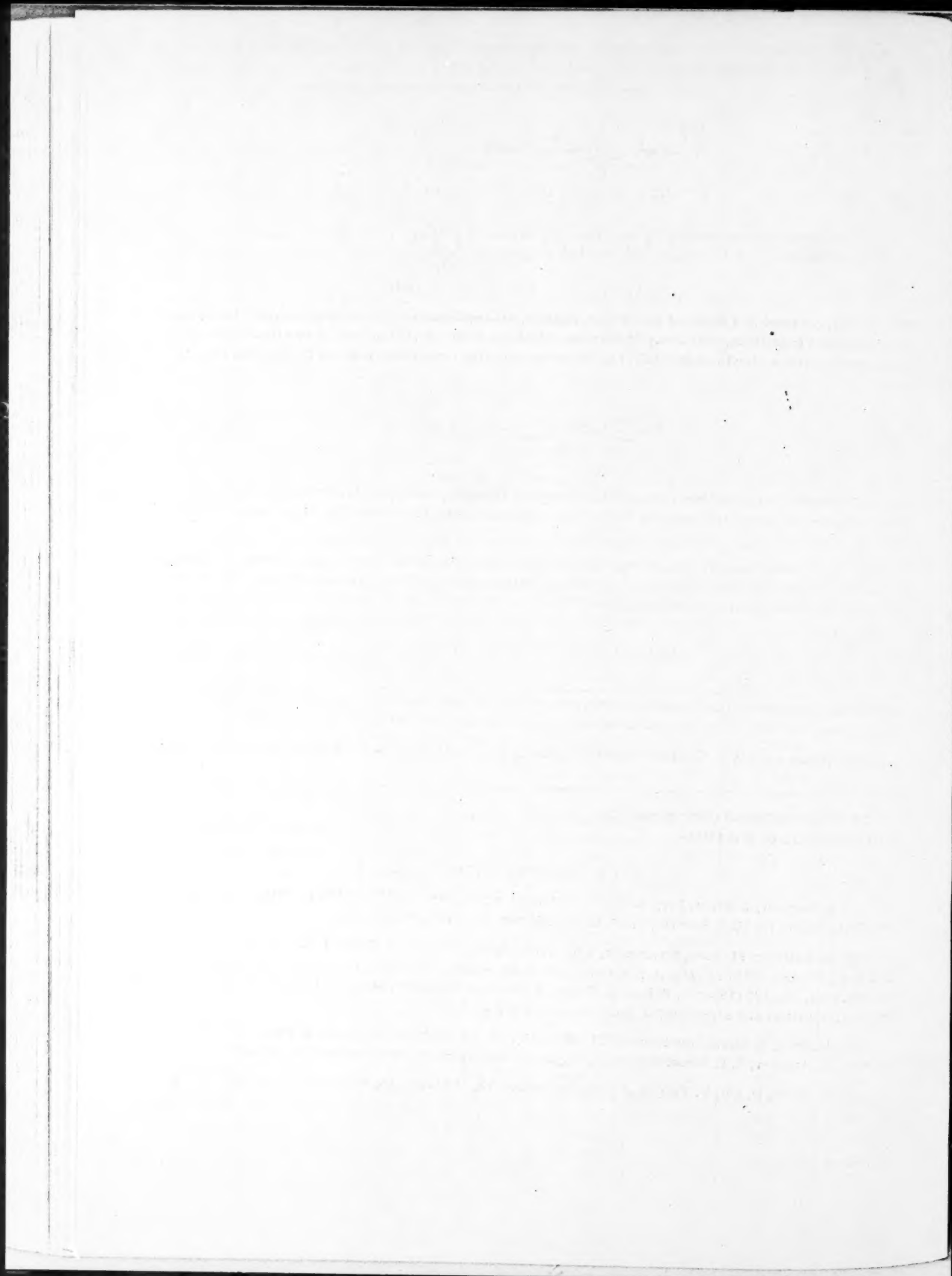
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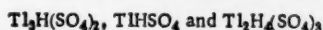


# CRYSTALLOGRAPHIC INVESTIGATION OF THE SULFATES OF MONOVALENT THALLIUM

N. I. Bashilova and M. N. Lyashenko

(Presented by Academician G. G. Urazov, December 6, 1956)

Three acid thallium sulfates are formed by the reaction of thallium sulfate with aqueous solutions of sulfuric acid [1]:



The starting substance,  $\text{Tl}_2\text{SO}_4$ , has been subjected to crystallographic [2] and X-ray [3,4] analysis. The acid sulfates of thallium, two of which were known previously [5,6], have only been subjected to qualitative crystallographic examination [5], while goniometric data are available for one of them [7].

$\text{Tl}_2\text{H}(\text{SO}_4)_2$  crystallizes in the form of thin plates belonging to the class of trigonal syngony [7]. We determined the refractive indices (Table 1) by the immersion method.

TABLE 1

Compound	Refractive indices			Angle of the optical axes
	$N_p$	$N_m$	$N_g$	
$\text{Tl}_2\text{H}(\text{SO}_4)_2$	1.730	1.760	—	—
$\alpha\text{-TIHSO}_4$	1.682	1.690	1.702	+78°
$\beta\text{-TIHSO}_4$	1.653	1.679	1.684	-45°
$\text{Tl}_2\text{H}_4(\text{SO}_4)_3$	—	1.619	—	—

$\text{TIHSO}_4$ , in agreement with the data of previous investigators [5,6,8], crystallizes in the forms of tetragonal plates and needles.

Both crystal forms do not alter their outward appearance when kept separately at rest and for a long period in a solution saturated with them. Crystals in the form of needles are developed in the solid phase, however, on prolonged stirring of the saturated solution containing lamellar crystals of thallium bisulfate. At the same time the plates disappear and change completely into needles.

It was necessary to establish whether thallium bisulfate is dimorphous, as claimed by the previous investigators [5,8,9], or whether the acicular and lamellar crystals of  $\text{TIHSO}_4$  belong to one and the same modification, in which the difference between outward forms is due to unequal development of the crystal faces.

The crystals of thallium bisulfate were examined by crystal optics and by goniometry. The single crystals required for this purpose were grown in hermetically closed crystallizers. Plates of thallium bisulfate were grown by slow crystallization from very slightly supersaturated solutions; needles were grown from separate and isolated, previously prepared, crystals. Goniometric measurement of the crystals was made difficult by their hygroscopicity which caused the faces to rapidly lose their luster. The quality of the signals was therefore moderate. The accuracy of measurement was  $\pm 1^\circ$ .

Results of the goniometric measurements are presented in Table 2.

The goniometric measurements indicate that the needles correspond to the rhombic syngony of the rhombodipyramidal form of symmetry. Elements of the crystal:  $a:b:c = 0.23:1:0.31$ . The following simple forms were observed on these crystals of thallium bisulfate:  $\{100\}$ ,  $\{110\}$ ,  $\{111\}$ . The right zone of the crystals consists of a broad pinacoid 100 and of a prism 110 with very narrow faces. The slanting zone consists of the 111 dipyramid.

TABLE 2

Crystals	Symbols of the faces	Designation of faces	$\rho_{\text{meas}}$	$\varphi^*$		No. of observations
				meas.	calc.	
Needles $\alpha$ -TiHSO <sub>4</sub>	100	a	90	90	—	8
	110	m	90	30	30	8
	111	n	21	30	—	8
Plates $\beta$ -TiHSO <sub>4</sub>	001	c	15	90	—	6
	010	b	90	0	—	4
	110	m	90	46	—	6

The crystal-optical investigation of the acicular crystals showed that these are biaxial positive crystals. They have right extinction. Their refractive indices, determined by the immersion method, and the angle of the optical axes (measured on the Fedorov stage) are presented in Table 1.

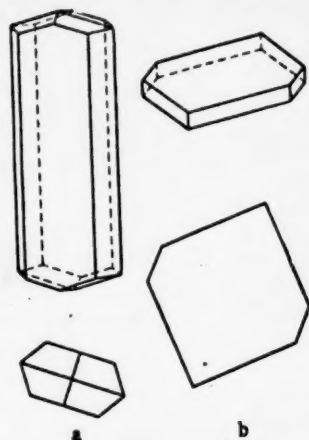


Fig. 1. General view of a crystal of  $\alpha$ -TiHSO<sub>4</sub> (a) and  $\beta$ -TiHSO<sub>4</sub> (b).

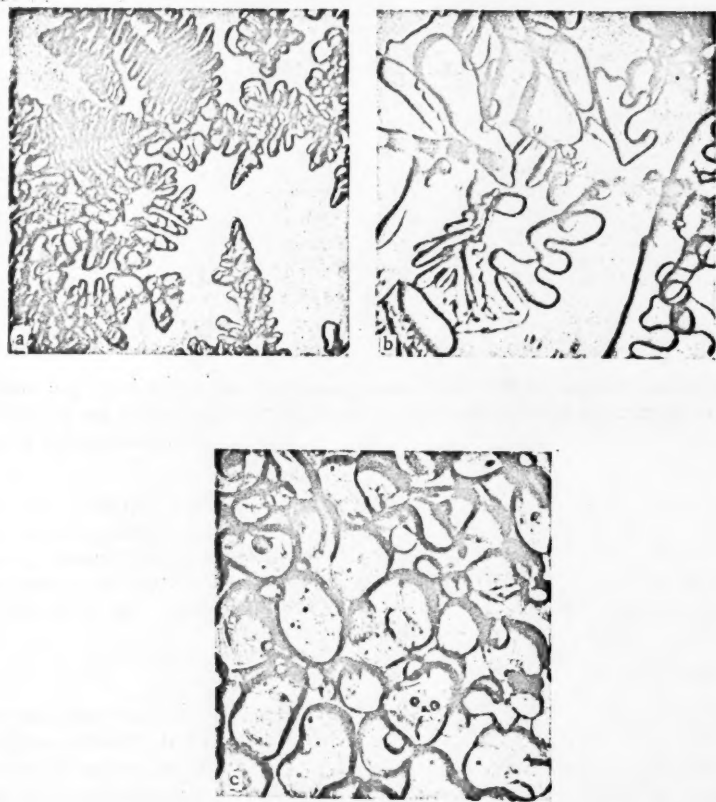


Fig. 2. Photomicrographs of  $\text{Ti}_2\text{H}_4(\text{SO}_4)_3$  at various stages of crystallization, 120x

The goniometric measurements indicate that the lamellar crystals of thallium bisulfate have monoclinic syngony with the prismatic form of symmetry.

Crystal elements:  $a : b : c = 0.98 : 1 : ?$ ,  $\beta = 105^\circ$ . Due to the insufficient number of developed faces, the parameters of the crystal could not be completely calculated. Slanting faces could not be observed on any of the crystals. These crystals of thallium bisulfate have the following simple forms:  $\{110\}$ ,  $\{001\}$ ,  $\{010\}$ .

Judging by the crystal-optical data, the lamellar crystals of thallium bisulfate are biaxial and negative. They possess both symmetrical and oblique extinction. The extinction angle is  $25^\circ$ . The refractive indices and the angle of the optical axes of these crystals are presented in Table 1.

The results set forth above show that in ordinary conditions thallium bisulfate crystallizes in two modifications—an acicular  $\alpha$ -modification and a lamellar  $\beta$ -modification (Fig. 1).

$Tl_2H_4(SO_4)_3$  crystallizes from very concentrated and viscous solutions [1] in which the normal growth of the crystals is hindered. Their form is therefore extremely incomplete. The progress of crystallization of  $Tl_2H_4(SO_4)_3$ , shown in Fig. 2, illustrates the formation of a granular microstructure (Fig. 2c) from the dendritic structure (2a and b).

Crystals of  $Tl_2H_4(SO_4)_3$  are isotropic. The refractive index of these crystals is given in Table 1.

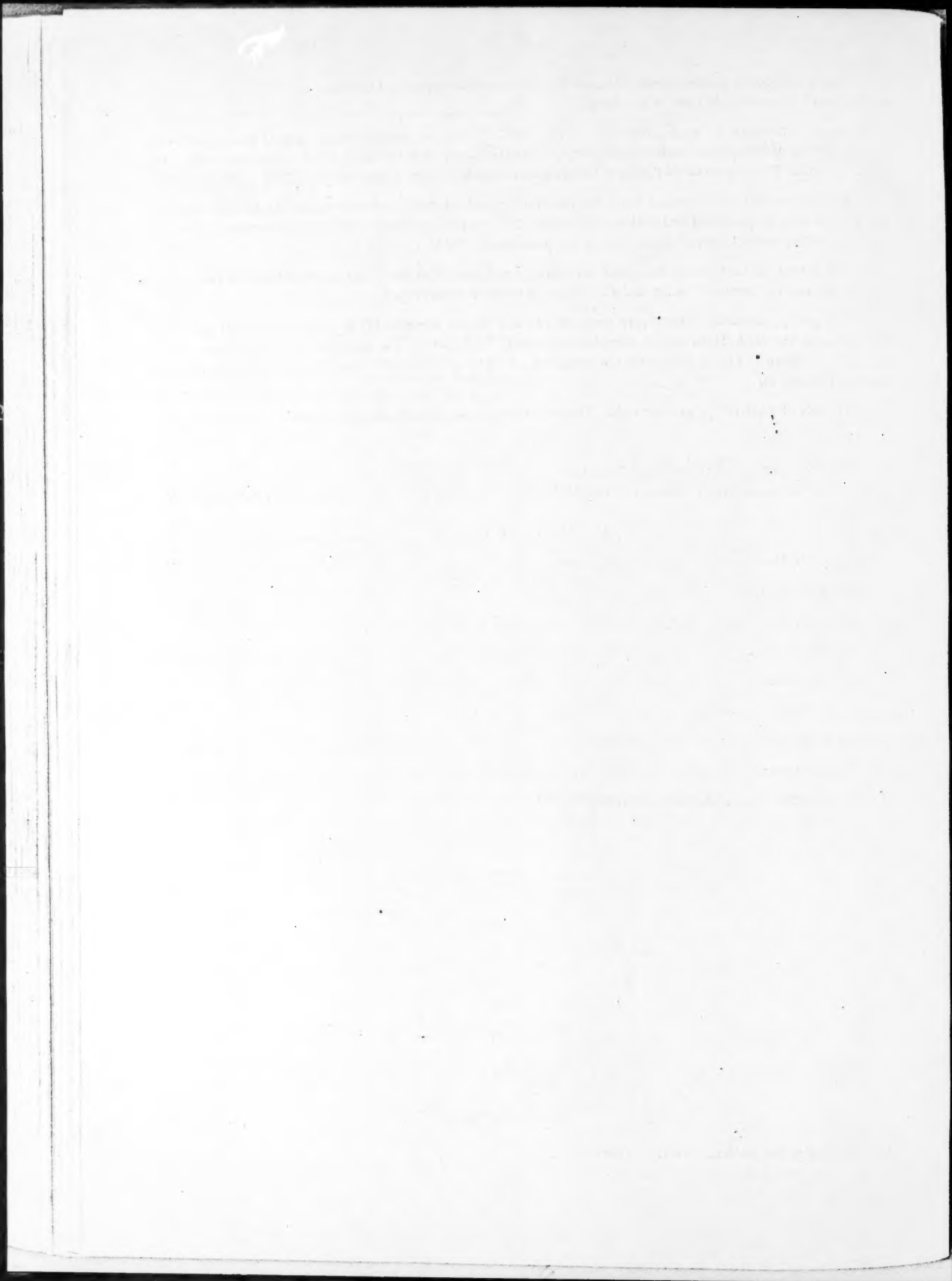
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# INVESTIGATION OF THE PHASE DIAGRAM OF THE SYSTEM RbF-BeF<sub>2</sub> AND ITS RELATION TO THE SYSTEM BaO-SiO<sub>2</sub>

N. G. Grebenshchikov

(Presented by Academician N. V. Belov, November 16, 1956)

Only two fluoride systems of the type of Me<sup>+</sup>F-BeF<sub>2</sub>, where Me<sup>+</sup> is an alkali element, have had their phase diagrams plotted; these are LiF-BeF<sub>2</sub> [1,2] and NaF-BeF<sub>2</sub> [3-5]. In the light of Goldschmidt's concepts, these may be regarded as weakened fluoride analogs of the silicate systems Mg(Zn)O-SiO<sub>2</sub> and CaO-SiO<sub>2</sub> respectively.

In order to fill the gap resulting from the absence of a fluoride analog of the system BaO-SiO<sub>2</sub>, it was of interest to examine the system RbF-BeF<sub>2</sub> (not previously investigated) with respect to its chemical compounds and phase diagram.

The phase diagram of the system RbF-BeF<sub>2</sub> was plotted with the help of differential-thermal, X-ray and crystal-optical data. 25 different compositions in the system were subjected to thermal examination; after each experiment the compositions were examined under the microscope in polarized light in immersion preparation\* for determination of the phase composition on the basis of the values of the refractive indices of the individual substances. Some of the mixtures (15; 40; 46.5; 60; and 75 mole % BeF<sub>2</sub> and also a few compositions) were examined by X-rays in order to obtain confirmation of the phase composition. The system RbF-BeF<sub>2</sub> (Fig. 1) consists of four separate eutectic systems; the starting substances for their thermal investigation were the terminal members of these partial systems. An exception is the system RbBe<sub>2</sub>F<sub>5</sub>-BeF<sub>2</sub> where BeF<sub>2</sub> was introduced into the starting mixtures in the form of the salt (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub>\*\* which breaks down to BeF<sub>2</sub> and gaseous NH<sub>4</sub>F in the temperature region of 220-380°.

The starting substances for the preparation of rubidium fluoroberyllates were Rb<sub>2</sub>CO<sub>3</sub> (pure for analysis) and (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub>. Three compounds were detected in the system: Rb<sub>2</sub>BeF<sub>4</sub>, RbBeF<sub>3</sub> and RbBe<sub>2</sub>F<sub>5</sub>. Rb<sub>2</sub>BeF<sub>4</sub> was first prepared by Mukherjee [6]; Novoselova and Simanov [7] reported the existence of RbBeF<sub>3</sub>; data for RbBe<sub>2</sub>F<sub>5</sub> are lacking in the literature. We prepared Rb<sub>2</sub>BeF<sub>4</sub> from an aqueous solution of equimolar amounts of Rb<sub>2</sub>CO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub>; RbBeF<sub>3</sub> and RbBe<sub>2</sub>F<sub>5</sub> were prepared by sintering Rb<sub>2</sub>BeF<sub>4</sub> and RbBeF<sub>3</sub> (each independently) with (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub> in 1:1 molar ratio in each case. RbF was obtained from Rb<sub>2</sub>CO<sub>3</sub> by displacing CO<sub>2</sub> with hydrofluoric acid. We have previously studied the polymorphism, structure and crystal-optical properties of Rb<sub>2</sub>BeF<sub>4</sub> and RbBeF<sub>3</sub> as fluoroberyllate analogs of Ba<sub>2</sub>SiO<sub>4</sub> and BaSiO<sub>3</sub> respectively. We confirmed the separate existences of ortho-, meta- and difluoroberyllates of rubidium by measurement of crystal-optical properties and by data for the lattice spacings of these compounds. Table 1 contains values of the refractive indices and densities and analytical data for (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub> and the three rubidium fluoroberyllates.

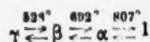
Difficulty was encountered in studying the partial eutectic system RbF-Rb<sub>2</sub>BeF<sub>4</sub> due to its hygroscopicity and the slight volatility of RbF. The latter was detected by chemical analysis of a mixture with the eutectic composition after thermal analysis. This evidently also accounts for the slight scatter of the points in that part of the system. The eutectic of the system RbF-Rb<sub>2</sub>BeF<sub>4</sub>, containing the congruently melting RbF (m.p. 770°) and Rb<sub>2</sub>BeF<sub>4</sub> (m.p. 807°), lies at 693° and has the composition 23 mole % BeF<sub>2</sub> + 77 mole % RbF. The solid-phase equilibrium in the system RbF-Rb<sub>2</sub>BeF<sub>4</sub> is characterized by the existence of 5 fields of stability of the

\* Due to the low refractive indices of fluoroberyllates, immersion liquids were prepared from methyl alcohol (n = 1.329) and glycerol.

\*\* The salt (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub> was prepared by the procedure of Novoselova and Averkova [10] from equimolar amounts of Be(OH)<sub>2</sub> • (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and hydrofluoric acid.



limited solid solutions of RbF in  $\text{Rb}_2\text{BeF}_4$  comprising: 1) 2 fields of stability of the phases  $\gamma$ -solid solution +  $\beta$ -solid solution (field 6-7-8) and  $\beta$ -solid solution +  $\alpha$ -solid solution (field 3-4-5) and 2) 3 fields of stability of  $\gamma$ -solid solution (field 9-6-8),  $\beta$ -solid solution (field 4-5-7-8) and  $\alpha$ -solid solution (field 1-2-3-4). The fields enumerated above are the consequence of the existence of three modifications:  $\gamma$ -,  $\beta$ - and  $\alpha$ - $\text{Rb}_2\text{BeF}_4$ , which undergo enantiotropic polymorphic transformations according to the scheme



and each forms limited solid solutions with RbF. The exact boundaries of existence of these equilibrium fields have not been established, and they are therefore indicated by broken lines. The presence, however, of limited solid solutions of RbF in the three modifications of  $\text{Rb}_2\text{BeF}_4$  is confirmed by the marked difference in the temperatures of the polymorphic transformations of pure  $\text{Rb}_2\text{BeF}_4$  in comparison with its limited solid solutions: for  $\gamma$ -solid solution  $\rightleftharpoons$   $\beta$ -solid solution  $556^\circ$ , for  $\beta$ -solid solution  $\rightleftharpoons$   $\alpha$ -solid solution  $672^\circ$ . The powder diagram of the composition containing 15 mole %  $\text{BeF}_2$  exhibits, apart from lines belonging to RbF and  $\gamma$ - $\text{Rb}_2\text{BeF}_4$ -solid solution, quite conspicuous lines that very probably relate to modifications of  $\beta$ -solid solution and  $\alpha$ - $\text{Rb}_2\text{BeF}_4$ -solid solution stabilized by solution of RbF in them. The values of  $N_{\text{comp}}$  of the different modifications of the solid solution of  $\text{Rb}_2\text{BeF}_4$  differ only slightly from the refractive index of  $\gamma$ - $\text{Rb}_2\text{BeF}_4$   $N_{\text{comp}} = 1.383$ ; hence the solubility of RbF in  $\gamma$ -,  $\beta$ - and  $\alpha$ - $\text{Rb}_2\text{BeF}_4$  can roughly be assumed equal to not more than 10-12 wt. % RbF (at high temperatures).

TABLE 1

Elements	$(\text{NH}_4)_2\text{BeF}_6$ ( $N = 1.307$ )		$\text{Rb}_2\text{BeF}_4$ (density 3.64, $N = 1.383$ )		$\text{RbBeF}_3$ (density 3.13, $N = 1.338$ )		$\text{RbBe}_2\text{F}_5$ (density 2.81, $N = 1.332$ )	
	exper.	theor.	exper.	theor.	exper.	theor.	exper.	theor.
Rb <sup>+</sup>	( $\text{NH}_4^+$ )	( $\text{NH}_4^+$ )	65.99	66.78	55.09	56.422	42.85	43.06
Be <sup>2+</sup>	7.54	7.45	3.61	3.57	5.92	5.954	9.19	9.09
F <sup>-</sup>	62.57	62.76	29.53	29.73	38.40	37.624	47.08	47.85
$\Sigma$	70.11	70.21	99.13	100.0	99.41	100.00	99.12	100.00

The portion of the system from 33.33 to 50 mole %  $\text{BeF}_2$  is the eutectic phase diagram of  $\text{Rb}_2\text{BeF}_4$ - $\text{RbBeF}_3$ , the eutectic of which has the composition 47.5 mole %  $\text{BeF}_2$  + 52.5 mole % RbF and lies at  $462^\circ$ .  $\text{RbBeF}_3$  melts congruently at  $465^\circ$ . In the field of separation of  $\text{Rb}_2\text{BeF}_4$  from the melt, the boundaries between the equilibrium fields of the  $\alpha$  and  $\beta$  modifications at  $692^\circ$  and between the  $\beta$  and  $\gamma$  modifications at  $528^\circ$  are represented by two broken horizontal lines. Three points corresponding to the thermal effects for the compositions 37 and 40 mole %  $\text{BeF}_2$  at a mean temperature of  $632^\circ$  represent, as previously noted [9], the transformation of  $\beta$ - $\text{Rb}_2\text{BeF}_4$  into  $\alpha'$ -form, which is stable at  $632$ - $692^\circ$  in presence of  $\text{RbBeF}_3$ . The absence of such a transformation from the system  $\text{RbF}$ - $\text{Rb}_2\text{BeF}_4$  does not allow us to represent it in the form of the corresponding equilibrium fields of the  $\alpha'$ -form in the phase diagram of the system. We postulate the existence in the system of a compound with the composition  $3\text{RbF} \cdot 2\text{BeF}_2$  which breaks down in the solid state at  $427^\circ$  to  $\gamma$ - $\text{Rb}_2\text{BeF}_4$  and  $\alpha$ - $\text{RbBeF}_3$ . The independent existence of the compound  $3\text{RbF} \cdot 2\text{BeF}_2$  could not be confirmed by the X-ray method; under the microscope mixtures of the system  $\text{Rb}_2\text{BeF}_4$ - $\text{RbBeF}_3$  were found to contain a small quantity of a phase whose refractive index was between that of  $\text{Rb}_2\text{BeF}_4$  and  $\text{RbBeF}_3$ . Compounds that decompose in the solid state are usually unstable; this evidently also accounts for the difficulty of obtaining  $3\text{RbF} \cdot 2\text{BeF}_2$  in quantity sufficient for X-ray confirmation of its chemical individuality. In one of the experiments the thermal effect at the composition  $3\text{RbF} \cdot 2\text{BeF}_2$  at  $322^\circ$  was caused by the  $\beta \rightleftharpoons \alpha$ -transformation of the  $\text{RbBeF}_3$  present. There is still no adequate explanation, however, of the development of a thermal effect with  $\text{RbBe}_2\text{F}_5$  at a temperature close to the temperature of polymorphic transformation of  $\text{RbBeF}_3$ . The high-temperature x-ray examination of  $\text{RbBe}_2\text{F}_5$  at 20, 200 and  $350^\circ$  did not reveal any appreciable change in structure if we ignore the thermal widening of the lattice. The horizontal line in the system  $\text{RbF}$ - $\text{BeF}_2$  for compositions of 40 to 66.66 mole %  $\text{BeF}_2$  at 316 represents the boundary of the fields of existence of the enantiotropic modifications of  $\text{RbBeF}_3$ , below which rhombic  $\beta$ - $\text{RbBeF}_3$  is in equilibrium and above which  $\alpha$ - $\text{RbBeF}_3$  is in equilibrium.



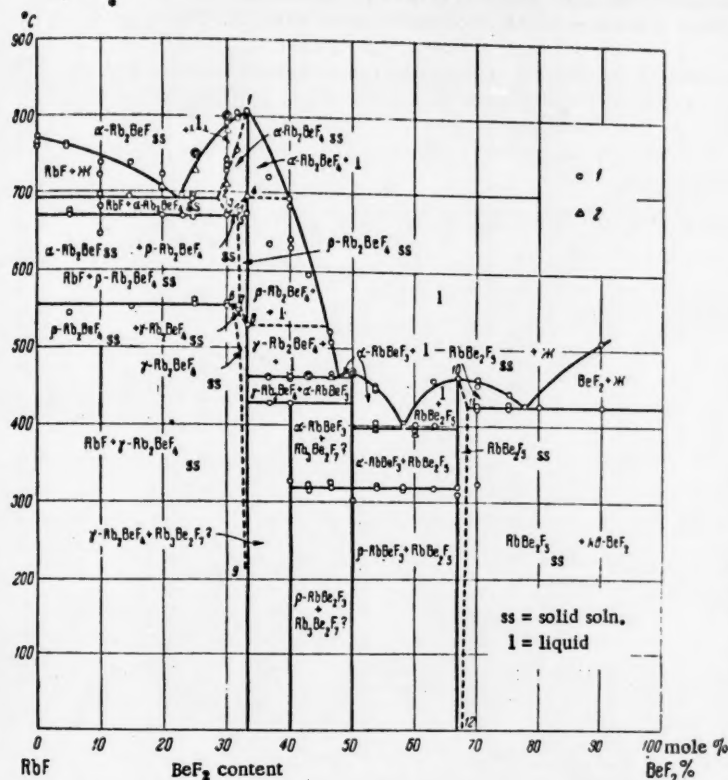


Fig. 1. Phase diagram of the system RbF-BeF<sub>2</sub>:  
1) temperatures of thermal effects on the heating thermograms,  
2) temperatures of thermal effects on the cooling thermograms.

The system RbF-BeF<sub>2</sub> in the range of compositions of 50 to 100 mole % BeF<sub>2</sub> consists of two simple eutectic diagrams of RbBeF<sub>3</sub>-RbBe<sub>2</sub>F<sub>5</sub> and RbBe<sub>2</sub>F<sub>5</sub>-BeF<sub>2</sub>, mixtures of the compounds of which crystallize in a eutectic composition corresponding to 58 mole % BeF<sub>2</sub> + 42 mole % RbF at 396° and 77.5 mole % BeF<sub>2</sub> + 22.5 mole % RbF at 425°. Crystals of RbBe<sub>2</sub>F<sub>5</sub> are biaxial, with a large angle of the optical axes with (-) optical sign and very weak double refraction. Complete cleavability along one of the planes and a tendency towards polysynthetic twinning is observed with crystals of RbBe<sub>2</sub>F<sub>5</sub>. The compound is readily hygroscopic, melts congruently at 462° and has a flat melting maximum. RbBe<sub>2</sub>F<sub>5</sub> forms limited solid solutions with BeF<sub>2</sub>; this was established by the changes in lattice spacing of the solid solution of RbBe<sub>2</sub>F<sub>5</sub> from a mixture of the composition 70 mole % BeF<sub>2</sub> in comparison with the  $d/n$  of pure RbBe<sub>2</sub>F<sub>5</sub>, and was also confirmed by the lowering of the refractive index of RbBe<sub>2</sub>F<sub>5</sub> solid solution which became lower than  $N = 1.329$ . The presence in the mixture with the composition 70 mole % BeF<sub>2</sub> of a very small amount of a second BeF<sub>2</sub> phase shows that the composition corresponding to the limited solubility of BeF<sub>2</sub> in RbBe<sub>2</sub>F<sub>5</sub> must lie between RbBe<sub>2</sub>F<sub>5</sub> and the composition with 70 mole % BeF<sub>2</sub>, as represented by the broken line on the diagram. A quartz-like modification of BeF<sub>2</sub> with extraordinarily low double refraction exists in the field of the partial diagram of RbBe<sub>2</sub>F<sub>5</sub>-BeF<sub>2</sub> below the eutectic temperature in equilibrium with the RbBe<sub>2</sub>F<sub>5</sub> solid solution.

BeF<sub>2</sub> gradually softens when heated and remains quite viscous; it also has a tendency to supercooling. Great experimental difficulties therefore arise in the determination of the character and the temperature of melting of BeF<sub>2</sub>. Kirkina, Novoselova and Simanov [11] report that BeF<sub>2</sub> starts to melt at 545° and finally fuses at about 740°, but the authors do not describe the character of its melting. In the construction of the phase diagram of the system RbF-BeF<sub>2</sub> the heterogeneity of melting of BeF<sub>2</sub> prevented us from plotting the liquidus of the separation of BeF<sub>2</sub> from the melt on the temperature ordinate characterizing the thermal behavior of BeF<sub>2</sub>.

Comparison of the "model" systems  $\text{RbF}-\text{BeF}_2$  and  $\text{BaO}-\text{SiO}_2$  and their phase diagrams shows that the compounds formed in the systems are similar in stoichiometry of composition, character of melting (congruent) and structure. In the phase diagrams of both systems the liquidus curves are similar in the interval of compositions from  $\text{RbF}$  to  $\text{RbBeF}_3$  in the fluoride system and from  $\text{BaO}$  to  $\text{BaSiO}_3$  in the silicate system. But the solid-phase equilibria in the system  $\text{RbF}-\text{BeF}_2$  are more complex than in the system  $\text{BaO}-\text{SiO}_2$ . The occurrence of polymorphism in  $\text{Rb}_2\text{BeF}_4$  and  $\text{RbBeF}_3$ , i.e., in the fluoride analogs of  $\text{Ba}_2\text{SiO}_4$  and  $\text{BaSiO}_3$ , suggests the possibility also of polymorphism in barium silicates, the existence of which might be overlooked due to the difficulty of reaching equilibrium states in silicate systems. The existence in the system  $\text{BaO}-\text{SiO}_2$  [12] of the compound  $2\text{BaO} \cdot 3\text{SiO}_2$  (forming continuous solid solutions with  $\text{BaSi}_2\text{O}_6$  and the absence of a compound of analogous formula in the system  $\text{RbF}-\text{BeF}_2$  calls for a check of the independent existence of the compound  $2\text{BaO} \cdot 3\text{SiO}_2$  a composition stoichiometrically close to  $2\text{BaO} \cdot 3\text{SiO}_2$ .

In conclusion we express our profound gratitude to Prof. N. A. Toropov for his scientific guidance in the investigation.

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Academy of Sciences of the USSR

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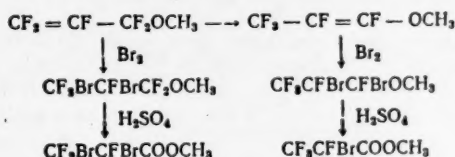
# THE ANIONOTROPIC REARRANGEMENT OF SUBSTITUTED PERFLUOROPROPENES

B. L. Dyatkin, L. S. German and Academician I. L. Knunyants

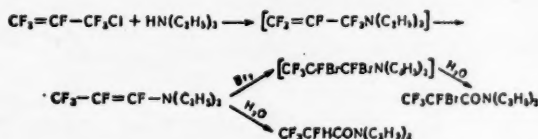
As we have shown [1], addition and vinyl substitution reactions compete in the interaction of perfluoropropene and perfluorobutylene with alcohols and amines. Allyl substitution is not observed, indicating that in the molecules of these fluoroolefins the effects of the conjugation of the double bond with the C-F bond in the  $\text{CF}_3$ - group is weakly manifested. Much interest is therefore attached to the reaction of chlorofluoropropenes and butenes, in particular of perfluoroallyl chloride  $\text{CF}_2=\text{CF}-\text{CF}_2\text{Cl}$ . It is reported [2] that reaction of nucleophilic reactants with perfluoroallyl chloride leads to substitution of chlorine for the corresponding anion, and this may be regarded as a consequence of the conjugation of the C-Cl bond with the double bond.

We investigated the reaction of perfluoroallyl chloride with sodium methoxide and diethylamine. Reaction with sodium methoxide leads to perfluoroallyl methyl ether whose structure was confirmed by bromination and subsequent hydrolysis to the methyl ester of  $\alpha, \beta$ -dibromoperfluoropropionic acid. This reaction is consequently a new route to derivatives of perfluoroacrylic acid.

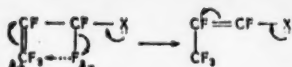
Perfluoroallyl methyl ether isomerizes to perfluoropropenyl methyl ether on keeping even at reduced temperature; the structure of the latter was confirmed by bromination followed by hydrolysis with formation of the methyl ester of  $\alpha$ -bromoperfluoropropionic acid.



Perfluoroallyl chloride readily reacts with diethylamine. The resultant perfluoroallyl-diethylamine rearranges to perfluoropropenyl-diethylamine during the reaction itself; hydrolysis of the latter gives the diethylamide of  $\alpha$ -hydroperfluoropropionic acid. Bromination of perfluoropropenyl-diethylamine and subsequent hydrolysis gives the diethylamide of  $\alpha$ -bromoperfluoropropionic acid.



The isomerization is an allylic rearrangement and is evidently the consequence of the tendency to form a more stable system at the expense of the conjugation of the double bond with the unshared electron pair of the substituent in the allyl position.



The speed of the rearrangement depends upon the mobility of the electron pair:

$\text{CF}_2=\text{CF}-\text{CF}_2\text{Cl}$	most stable - no rearrangement observed
$\text{CF}_2=\text{CF}-\text{CF}_2\text{OCH}_3$	relatively stable - rearranges in storage
$\text{CF}_2=\text{CF}-\text{CF}_2\text{N}(\text{C}_2\text{H}_5)_2$	completely unstable - rapidly rearranges

## EXPERIMENTAL

**Perfluoroallyl methyl ether.** A solution of sodium methoxide, prepared from 4.6 g (0.20 g-atom) sodium and 100 ml absolute methanol, was added by drops with stirring to a solution of 59 g (0.35 mole) perfluoroallyl chloride in 100 ml absolute methanol (containing phenolphthalein) with cooling to  $-10$  to  $-15^\circ$ . Addition was made at such a rate that the alkali could react. After completion of the addition, the unreacted olefin was distilled off and the reaction mixture was run into water. The oily layer was dried over calcium chloride and distilled. A small amount of original olefin (total weight 16 g) first came over and was followed at  $30-41^\circ$  (765 mm) by perfluoroallyl methyl ether; the main bulk of the latter came over at  $38-41^\circ$  (765 mm). Yield 21.8 g (67% of theory or 52% reckoned on the olefin consumed). Redistillation gave a substance with b.p.  $38.5^\circ$ ,  $n_D^{20}$  1.30000,  $d_4^{20}$  1.3683. Found  $\text{MR}_D$  21.91, calculated for  $\text{C}_4\text{F}_5\text{H}_3\text{O}$   $\text{MR}_D$  22.55. Literature data [2]: b.p.  $38.5^\circ$ ,  $n_D^{20}$  1.296,  $d_4^{20}$  1.358.

Found %: C 29.55; H 1.87  $\text{C}_4\text{F}_5\text{H}_3\text{O}$ . Calculated %: C 29.64; H 1.86

**$\beta$ ,  $\gamma$ -Dibromoperfluoropropyl methyl ether.** Prepared in a yield of 82% of theory by the action of excess dry bromine on perfluoroallyl methyl ether with cooling with ice water. Boiling point  $136-138^\circ$  (764 mm); after redistillation the product had b.p.  $136^\circ$ ,  $n_D^{20}$  1.4090,  $d_4^{20}$  2.1136. Found  $\text{MR}_D$  37.36, calculated for  $\text{C}_4\text{F}_3\text{Br}_2\text{H}_3\text{O}$   $\text{MR}_D$  38.54.

Found %: C 14.45; H 0.93  $\text{C}_4\text{F}_3\text{Br}_2\text{H}_3\text{O}$ . Calculated %: C 14.92; H 0.94

**Methyl ester of  $\alpha$ ,  $\beta$ -dibromoperfluoropropionic acid.** A mixture of 10 g of dibromoperfluoropropyl methyl ether, 4 ml conc.  $\text{H}_2\text{SO}_4$  and 4 g powdered glass was heated with stirring for 5 hours to  $100-105^\circ$ . Working up in the usual manner gave 7.2 g (77% of theory) of the methyl ester of  $\alpha$ ,  $\beta$ -dibromoperfluoropropionic acid with b.p.  $63-65^\circ$  (22 mm). The substance was redistilled before analysis and determination of constants: b.p.  $70.5^\circ$  (28 mm),  $n_D^{20}$  1.4380,  $d_4^{20}$  2.0598. Found  $\text{MR}_D$  38.23, calculated for  $\text{C}_4\text{F}_3\text{Br}_2\text{H}_3\text{O}_2$   $\text{MR}_D$  38.27.

Found %: C 15.92; H 1.06  $\text{C}_4\text{F}_3\text{Br}_2\text{H}_3\text{O}_2$ . Calculated %: C 16.01; H 1.00

**$\alpha$ ,  $\beta$ -Dibromoperfluoropropionamide.** Prepared from the methyl ester of the acid by the action of an aqueous alcoholic solution of ammonia, M.p.  $61.5-62.5^\circ$  (from n-hexane). The literature [3] reports m.p.  $60.6-61.6^\circ$ .

Found %: C 12.70; H 0.87; F 20.13; Br 56.11; N 5.06  $\text{C}_3\text{F}_3\text{Br}_2\text{H}_2\text{ON}$ .  
Calculated %: C 12.64; H 0.71; F 20.00; Br 56.10; N 4.91

**Perfluoropropenyl methyl ether.** This compound is formed as a result of spontaneous isomerization of perfluoroallyl methyl ether on standing for a few days. B.p.  $52.0-52.5^\circ$ ,  $n_D^{20}$  1.3045,  $d_4^{20}$  1.3605. Found  $\text{MR}_D$  22.44, calculated for  $\text{C}_4\text{F}_5\text{H}_3\text{O}$   $\text{MR}_D$  22.55.

Found %: C 29.29; H 1.97; F 58.92  $\text{C}_4\text{F}_5\text{H}_3\text{O}$ . Calculated %: 29.64; H 1.86; F 58.61

**$\alpha$ ,  $\beta$ -Dibromoperfluoropropyl methyl ether.** Prepared in 87% yield by the action of dry bromine on

\* Compound prepared by hydrolysis of  $\text{CF}_2\text{BrCFBrCN}$ .

perfluoropropenyl methyl ether while cooling with ice water. B.p. 134° (736 mm),  $n_D^{20}$  1.4040,  $d_4^{20}$  2.0510,  $MR_D$  found 38.41, calculated for  $C_4F_5Br_2H_3O$   $MR_D$  38.54. Literature [1]: b.p. 128-132° (732 mm).

Found %: C 15.20; H 0.97  $C_4F_5BrH_3O$ . Calculated %: C 14.92; H 0.94

Methyl ester of  $\alpha$ -bromoperfluoropropionic acid. Prepared by hydrolysis of  $\alpha,\beta$ -dibromoperfluoropropyl methyl ether, as we have previously described [1]. Yield 56%, b.p. 101-108°,  $n_D^{20}$  1.3592. Literature [1]: b.p. 105-107°,  $n_D^{20}$  1.3620.

$\alpha$ -Bromoperfluoropropionamide. Obtained from the methyl ester of the acid by the action of conc. aqueous solution of ammonia; m.p. 89.5-90.5° (from n-hexane). A mixture with an authentic sample melted without depression. The literature [1] gives m.p. 90.0-90.5°.

Perfluoropropenyl-diethylamine. A solution of 11 g (0.15 mol) diethylamine in 30 ml absolute ether was added to a solution of 16.6 g (0.1 mole) perfluoroallyl chloride in 50 ml absolute ether at -30 to -25° with intensive stirring over a period of 2 hours. After 30 minutes, when the temperature of the mixture had risen to room temperature, the precipitate of diethylamine hydrochloride was filtered off; the ether was driven off, and the residue distilled in vacuum in a stream of dry air. Yield 7.2 g (47%) of perfluoropropenyl-diethylamine in the form of a mobile liquid with an unpleasant odor, very easily hydrolyzed in the air. B.p. 56-59° (49 mm),  $n_D^{20}$  1.3715. Hydrolysis of perfluoropropenyl-diethylamine gave the diethylamine of  $\alpha$ -hydroperfluoropropionic acid with b.p. 67.5-68.0° (5 mm) and  $n_D^{20}$  1.3938. The literature [1] reports b.p. 89° (22 mm) and  $n_D^{20}$  1.3910. The identity of the prepared compound with an authentic specimen was confirmed by the method of nuclear magnetic resonance.

Diethylamide of  $\alpha$ -bromoperfluoropropionic acid. To a solution of 6.4 g of perfluoropropenyl-diethylamine in 30 ml dry methylene chloride was added an excess of dry bromine in the same solvent. After holding for half an hour at room temperature, the mixture was run into water, and the organic layer was washed with sodium bisulfite solution and with water and dried over calcium chloride. After removal of the solvent, the residue was distilled in vacuum to give 5.4 g (61% of theory) of the diethylamide of  $\alpha$ -bromoperfluoropropionic acid with the constants: b.p. 98-99° (23 mm),  $n_D^{20}$  1.4200,  $d_4^{20}$  1.5042. Found  $MR_D$  47.12, calculated for  $C_7F_4BrH_3ON$   $MR_D$  46.63.

Found %: C 30.23; H 3.54; N 5.31; Br 28.53; F 27.72  $C_7F_4BrH_3NO$ .

Calculated %: C 30.01; H 3.59; N 5.00; Br 28.53; F 27.13.

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\*Original Russian pagination. See C.B. translation.

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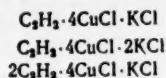
# THE ROLE OF COMPLEX COMPOUNDS AND CATIONS OF COMPLEX-FORMING COMPONENTS IN THE POLYMERIZATION OF ACETYLENE

A.L. Klebansky, I.M. Dolgopolsky and Z.F. Dobler

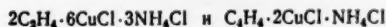
(Presented by Academician B.A. Kazansky, January 19, 1957)

The mechanism of the polymerization of acetylene cannot be said to be fully clarified [1, 2]. Investigation of the conditions of formation of complex compounds of acetylenic hydrocarbons with  $\text{CuCl-MCl}$  solutions and of the role of the individual components of the solutions in the course of polymerization has established the importance of complex compounds in catalytic reactions and has confirmed the ionic mechanism of the polymerization of acetylene [3].

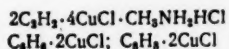
Due to the mobility of the  $\pi$ -electrons, acetylenic compounds are readily polarized by the central atom of copper which enters into complex compounds, displacing the chlorine atoms from the coordination sphere of copper and taking their place. Formation of complex compounds of acetylenic hydrocarbons in  $\text{CuCl-MCl}$  solutions is also confirmed by the considerable increase in solubility of acetylene and vinylacetylene and the simultaneous rise in solubility of  $\text{CuCl}$ , as well as by the subsequent separation from the solution of crystalline precipitates containing hydrocarbons in the form of complexes. Investigation of the composition of the complexes shows that they vary in dependence on the nature of the cation of the  $\text{MCl}$ , on the  $\text{CuCl:MCl}$  ratio in the solution and on the nature of the acetylenic hydrocarbon. Thus, for complex compounds of acetylene obtained in  $\text{CuCl-KCl}$  solution, Chavastelon [4] and Tsyurikh and Ginzburg (3a) proposed the following composition:



The latter authors put forward the following composition for the complex compounds formed by acetylene and vinylacetylene in  $\text{CuCl-NH}_4\text{Cl}$ , on the basis of analytical data for the mother liquor and the crude precipitate:



We prepared these complex compounds in the pure state and confirmed the composition proposed by Tsyurikh and Ginzburg. We also isolated a complex compound of acetylene from  $\text{CuCl-CH}_3\text{NH}_2\text{HCl}$  solution as well as complex compounds formed by divinylacetylene and acetylene tetramer. These compounds correspond to the following empirical formulas:



A study of the properties of all the above-mentioned complex compounds in the crystalline state showed

that they can be arranged in the following order in respect of thermal stability and speed of formation (in dependence on the nature of the hydrocarbon):  $C_2H_2 > C_4H_4 > C_6H_6 > C_8H_8$ ; thus the complex compounds of acetylene are the most stable.

It was established that the hydrogen ion concentration rises in CuCl-MCl solutions when acetylene is dissolved in them (Fig. 1A); this is due to ionization of the acetylenic hydrocarbons.

In the limiting case, ionization of acetylene takes place with dissociation of two hydrogen atoms of acetylene, while that of vinylacetylene takes place with dissociation of one atom. The hydrogen ion concentration of solutions of CuCl-MCl does not alter during formation of complex compounds of divinylacetylene and acetylene tetramer. It was observed that polymerization of vinylacetylene is accompanied by lowering of the hydrogen ion concentration, and at the close of polymerization the pH of the solution corresponds to the pH of the original CuCl-MCl solution. The degree of ionization of acetylenic hydrocarbons is governed not only by their nature but also by the composition of the original CuCl-MCl solution, as well as by the concentration of the components in solution.

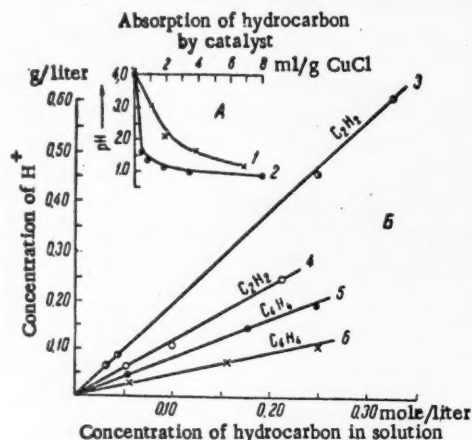


Fig. 1. Change of pH of CuCl-MCl solution on absorption of acetylenic hydrocarbons (A) and change of concentration of hydrogen ions in CuCl-MCl solution of absorption of acetylenic hydrocarbons as a function of the concentration of components in solution (B). 1)  $C_4H_4$ ; 2)  $C_2H_2$ ; 3) 5 M CuCl, 5  $MNH_4Cl$ ; 4) 2.5 M CuCl, 5  $MNH_4Cl$ ; 5) 5.0 M CuCl, 5  $MNH_4Cl$ ; 6) 2.5 M CuCl, 5  $MNH_4Cl$ .

With increasing concentration of MCl, i.e., of chlorine ions which displace acetylene from the complex, the degree of ionization falls. The degree of ionization is also a function of the acidity of the medium; the degree of ionization falls with increasing concentration of HCl in the original solution.

All these phenomena can be explained on the basis of concepts of the existence of a dynamic equilibrium between cation, chlorine ions and hydrogen ions. Increase of concentration of chlorine ions in the solution implies displacement of acetylene from the coordination sphere of copper and therefore a fall of its concentration in solution; the degree of ionization of dissolved acetylene is correspondingly reduced.

A much greater influence is exercised by the rise of HCl concentration in solution because, in addition to the influence of the chlorine ions, complex compounds of another composition containing HCl are formed.

A close relation was established between the susceptibility to ionization of complex compounds and the catalytic activity of their solutions. Catalytic activity increases with increasing degree of ionization of hydrogen in the hydrocarbon. The rate of polymerization of acetylene changes in proportion to the change in degree of ionization under the influence of various factors. As was established above, the degree of ionization of acetylene depends on the pH of the medium.

The effect of the acidity of the CuCl-MCl solution on the degree of ionization on the rate of polymerization of acetylene is illustrated in Fig. 2.

The role of water should be noted. This consists in hydration of the ions with formation of complex compounds due to which the catalytic activity of CuCl-MCl solutions is enhanced. In the absence of water, ionization of the complex compounds does not take place and the acetylene in turn is not polymerized. Thus, for example, acetylene was recovered completely from an anhydrous complex of acetylene maintained at 20° for 960 hours, whereas in the presence of even traces of moisture (air-dry complex) 5% of the acetylene polymerized in 48 hours.

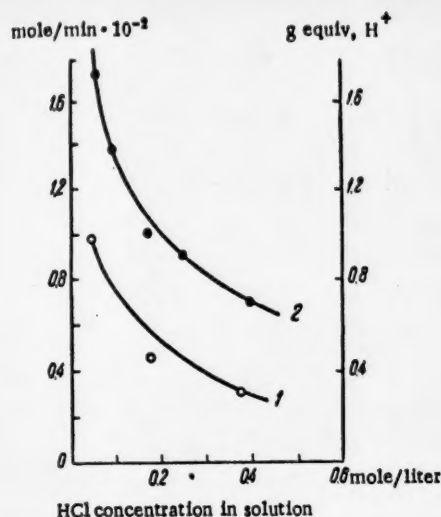


Fig. 2. Influence of acidity of solution of CuCl-MCl on the degree of ionization and rate of polymerization of acetylene: 1) degree of ionization of  $C_2H_2$ ; 2) rate of polymerization of  $C_2H_2$ .

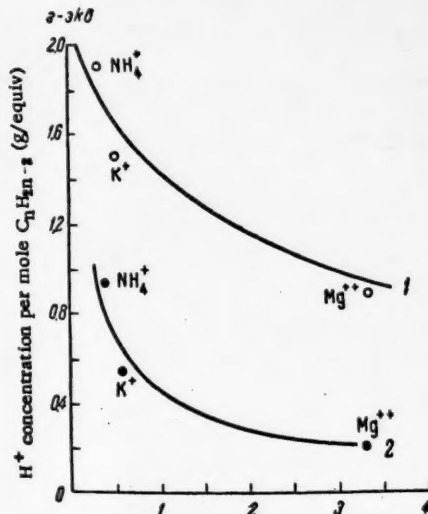
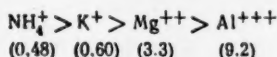


Fig. 3. Effect of strength of the cationic field (MCl) on the degree of ionization of acetylene and vinylacetylene in CuCl-MCl solution.

All the foregoing facts support the ionic mechanism of the processes of polymerization of acetylene.

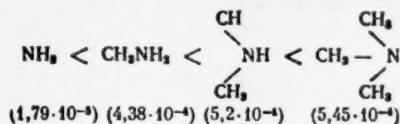
The composition and properties of complex compounds formed by acetylene and vinylacetylene with  $CuCl \cdot MCl$  and their catalytic activity depend, apart from the factors considered above, on the nature of the  $M^+$  cation of the complex-forming component (MCl). The following correlations were established in respect of the influence of the  $M^+$  cation: the higher the field strength of the cation the greater its influence on the properties of the complex compounds (solubility of CuCl and hydrocarbons, susceptibility to polymerization, activity during the process of polymerization of acetylene).

These properties diminish with increasing field strength of cations in the following sequence (field strength in brackets):



The relation between degree of ionization of complex compounds of acetylene and vinylacetylene and the field strength of the cation is shown in Fig. 3.

Salts of amines can also be used as complex-forming components (MCl). The polarity of amines is known to rise with increasing degree of substitution. This is accompanied by a corresponding change in their influence on composition, on the properties of the complex compounds and on the catalytic activity of their solutions. Amines may be arranged in the following series with respect to the degree of polarity which is characterized by the dissociation constant (dissociation constants in brackets):



The relation between catalyst activity and nature of the amine is plotted in Fig. 4 which shows that the transformation of vinylacetylene into acetylene tetramer is intensified with falling molecular weight of the cation; in the above series this may be characterized by the polarity of the cations of salts of amines, the activity of the catalysts falling with increasing polarity.

The influence of the nature of the cations is explained by their polarizing action on acetylenic hydrocarbons which is in the opposite direction to the influence of the charge of the central copper atom. The antipolarizing effect of the  $M^+$  cations in MCl is the greater the higher the field strength of the cation or its positive polarity for salts of amines.

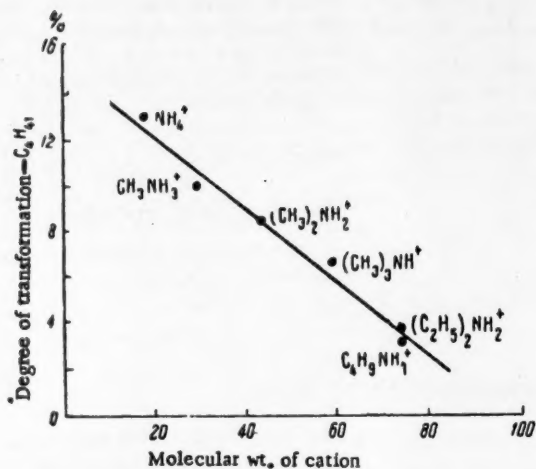


Fig. 4. Activity of catalytic solution of CuCl-MCl in dependence on the nature of the cation (MCl).

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# THE SYNTHESIS AND ISOMERIZATION OF ENOLACETATES OF β-FURANIDONES

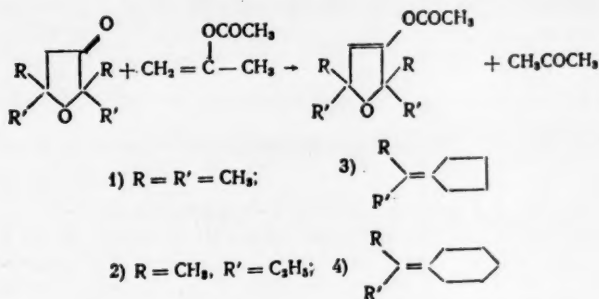
I. K. Korobitsyna, I. G. Zhukova, V. A. Kuvshinova,

N. N. Gaidamovich and Yu. K. Yuryev

(Presented by Academician B. A. Kazanski January 16, 1957)

Derivatives of the enol form of tetrahydrofuranone-3 (β-furanidone) and its homologs have scarcely been studied, and only Dupong [1] has pointed out that 2,2,5,5-tetramethylfuranidone-3 gives a sulfate of the enol form (under the action of sulfuric acid) and a sodium derivative of the enol form (under the action of metallic sodium); treatment of the latter compound with ethyl bromide gave 3-ethoxy-2,2,5,5-tetramethylidihydrofuran.

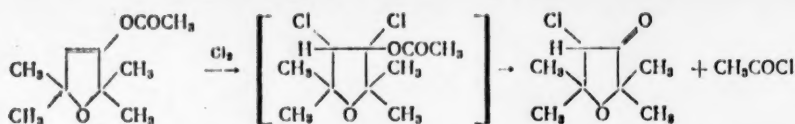
In the present work (on the preparation of acetyl derivatives of the enol form), use was made of ketones of the β-furanidone series in which only one methylene group was present in the α-position to the carbonyl group; this allowed the formation of only one enolacetate with the position of the double bond already known. The acetylating medium was isopropenyl acetate [2]. We established that in this case the acetates of the enol form of ketones of the β-furanidone series are formed in 65-85% yield, calculated on the ketone going into reaction (acylation with acetic anhydride was unsuccessful). In this manner we prepared the enol acetates of: 2,2,5,5-tetramethylfuranidone-3 (75.5%), 2,5-dimethyl-2,5-diethylfuranidone-3 (66%), 2,2,5,5-bis(4-methylenefuranidone-3) (80%) and 2,2,5,5-bis(pentamethylenefuranidone-3) (84.5%).



This type of interesting derivative of β-furanidones had not previously been described in the literature. It should be noted that in 1940 Yu. S. Zalkind and V. I. Baranov [3] studied the addition of acetic acid to tetramethylbutynediol in presence of mercury salts. Solely on the basis of analytical data, they erroneously assigned to one of the reaction products (m.p. 30.5-31° b.p. 88-96° at 6.5 mm) the structure of 2,2,5,5-tetramethylfuranidone-3.

We also studied the behavior of the enol acetates, which we prepared, halogenation and isomerization. It was found that passage of chlorine at -5° into the enol acetate of 2,2,5,5-tetramethylfuranidone-3 or its solution in chloroform or absolute ether gives a 67% yield of an α-monochloro ketone of the furanidine series, 4-chloro-2,2,5,5-tetramethylfuranidone-3, whose formation may be represented by the following scheme:



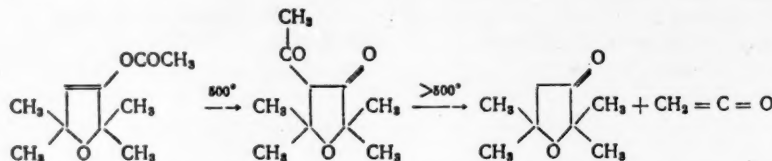


This reaction, although of theoretical interest, has no preparative importance since  $\alpha$ -chloro ketones of the furanidone series are obtained in good yield by direct chlorination of the corresponding ketones [4].

One of the most interesting reactions of enol acetates of ketones is their isomerization (thermal or catalytic) to  $\beta$ -diketones. Thus, for example, isopropenyl acetate isomerizes to acetylacetone in 70-83% yield when treated with boron trifluoride or passed through a quartz tube at 450-500° [5].

We established that isomerization does not take place when boron trifluoride is passed into the enol acetate of 2,2,5,5-tetramethylfuranidone-3 at -40 to -20°, whereas at -10 to -5°, following a short induction period, a violent reaction occurs with complete resinification of the reaction mixture.

On passing the enol acetate of 2,2,5,5-tetramethylfuranidone-3 through a quartz tube filled with glass wool and heated to 500°, isomerization to 4-acetyl-2,2,5,5-tetramethylfuranidone-3 takes place (yield 36.3%). This thermal isomerization proceeds in a very narrow temperature interval and after heating for a definite and very short period. Isomerization does not take place at lower temperatures (450-480°); at higher temperatures (510-520°) the yield of 4-acetyl-2,2,5,5-tetramethylfuranidone falls to 5-10% due to its cleavage into ketone and ketene:



Its structure is confirmed by the preparation of the copper salt and of derivatives of 4-acetyl-2,2,5,5-tetramethylfuranidone-3, as well as by the deep violet color imparted by a solution of ferric chloride. The absorption spectrum of the copper salt of 4-acetyl-2,2,5,5-tetramethylfuranidone-3 ( $\lambda_{\text{max}}$  256; 305 m $\mu$ ) is similar to the absorption spectrum of the copper salt of acetylacetone ( $\lambda_{\text{max}}$  240; 294 m $\mu$ ) characteristic of a  $\beta$ -diketone.

The study of the properties of this class of  $\beta$ -diketones of the furanidone series is being continued.

#### EXPERIMENTAL

**Enol acetate of 2,2,5,5-tetramethylfuranidone-3.** A mixture of 20 g isopropenyl acetate, 28.4 g 2,2,5,5-tetramethylfuranidone-3 [1] and 1.5 g *p*-toluenesulfonic acid was heated in a flask with a column 50 cm high and a sloping condenser until 12.5 ml acetone (86%) had distilled off. While cooling, the mixture was saturated with anhydrous sodium acetate, allowed to stand for a few hours and filtered. The precipitate was washed with absolute ether. The ether was driven off from the combined filtrates and the residue was twice fractionated to give 9.7 g of unchanged ketone and 18.3 g of the enol acetate of 2,2,5,5-tetramethylfuranidone-3 (50% on the ketone taken and 75.5% on the reacted ketone: b.p. 77-78° (19 mm);  $n_D^{20}$  1.4313;  $d_4^{20}$  0.9858;  $MR_D$  48.40;  $C_{10}H_{16}O_3$ . Calculated  $MR_D$  49.01;  $EM_D$  0.61.

Found %: C 65.10; 64.94; H 8.85; 8.79  $C_{10}H_{16}O_3$ . Calculated %: C 65.13; H 8.75

**Enol acetate of 2,5-dimethyl-2,4-diethylfuranidone-3** was prepared as described above from 17 g 2,5-dimethyl-2,5-diethylfuranidone-3 [1], 20 g isopropenyl acetate and 1.5 g *p*-toluenesulfonic acid; b.p. 105-107° (19 mm);  $n_D^{20}$  1.4441;  $d_4^{20}$  0.9634;  $MR_D$  58.54;  $C_{12}H_{20}O_3$ . Calculated:  $MR_D$  58.25;  $EM_D$  0.29.

Found %: C 68.39; 68.26; H 9.61; 9.73  $C_{12}H_{20}O_3$ . Calculated %: C 67.89; H 9.50



Enol acetate of 2,2,5,5-bistetramethylenefuranidone-3 was prepared as described above from 19.4 g 2,2,5,5-bistetramethylenefuranidone-3 [6], 20 g isopropenyl acetate and 10 drops of concentrated sulfuric acid; b.p. 124-127° (9 mm) m.p. 49° (from alcohol).

Found %: C 71.14; 71.22; H 8.93; 8.98  $C_{14}H_{20}O_3$ . Calculated %: C 71.16; H 8.53

Yield 9.8 g (41.5% on the ketone taken and 80% on the reacted ketone).

Enol acetate of 2,2,5,5-bispentamethylenefuranidone-3 was prepared as described above from 22.2 g 2,2,5,5-bispentamethylenefuranidone-3 [6], 20 g isopropenyl acetate and 10 drops of concentrated sulfuric acid; m. p. 54-55° (from alcohol).

Found %: C 72.69; 72.87; H 9.30; 9.20  $C_{16}H_{24}O_3$ . Calculated %: C 72.69; H 9.15

Yield 11 g (41.7% of the ketone taken and 84.5% of the reacted ketone).

Chlorination of the enol acetate of 2,2,5,5-tetramethylfuranidone-3. A stream of dry chlorine was passed into 11.5 g of 2,2,5,5-tetramethylfuranidone-3, while cooling to -5°, until the weight increase was 4.4 g. The reaction mass (which violently evolved hydrogen chloride in the air) was distilled in a nitrogen stream in vacuum to give 7.3 g (67%) of 4-chloro-2,2,5,5-tetramethylfuranidone-3; b.p. 65-66 g (8 mm);  $n_D^{20}$  1.4470;  $d_4^{20}$  1.0820;  $MR_D$  43.61;  $C_8H_{13}O_2Cl$ . Calculated  $MR_D$  43.83;  $EM_D$  0.22.

Found %: Cl 20.23; 20.17  $C_8H_{13}O_2Cl$ . Calculated %: Cl 20.07

Literature data: b.p. 184.5° (760 mm);  $n_D^{18}$  1.447;  $d^{18}$  1.0925 [4]. Similar results were obtained on chlorination in a medium of chloroform and absolute ether.

Preparation of 4-acetyl-2,2,5,5-tetramethylfuranidone-3. 14.5 g of the enol acetate of 2,2,5,5-tetramethylfuranidone-3 was passed at a speed of 3.75 ml/hour through a quartz tube filled with glass wool (internal diameter 10 mm, length of heated zone 100 mm) and heated to 500°. Distillation of the product of isomerization in vacuum gave 7.2 g of unchanged enol acetate. Addition to the residue of 20 ml of a saturated solution of copper acetate resulted in isolation of 3.1 g (36.8%) of the copper salt of 4-acetyl-2,2,5,5-tetramethylfuranidone-3; b.p. 285° (from alcohol).

Found %: 55.52; 55.37; H 7.11; 7.19  $C_{20}H_{30}O_6Cu$ . Calculated %: C 55.86; H 7.03

Decomposition of 3.1 g of the copper salt of 4-acetyl-2,2,5,5-tetramethylfuranidone-3 with 20% sulfuric acid gave 2.5 g (94%) of 4-acetyl-2,2,5,5-tetramethylfuranidone-3; m.p. 53° (from absolute alcohol). On standing in the air it rapidly changed into the hydrate with m.p. 73°.

Found %: C 59.57; 59.62; H 9.08; 9.10  $C_{10}H_{16}O_3 \cdot H_2O$ . Calculated %: C 59.39; H 8.97

Semicarbazone: m.p. 156-157° (from cyclohexane).

Found %: C 54.72; 54.98; H 7.96; 8.17  $C_{11}H_{19}O_3N_3$ . Calculated %: C 54.76; H 7.93

Phenylhydrazone: m.p. 151° (from alcohol).

Found %: C 70.49; 69.78; H 8.29; 8.12; N 10.15; 10.36  $C_{16}H_{22}O_2N_2$ . Calculated %: C 70.04; H 8.08; N 10.21

Moscow State University, by M. V. Lomonosova.

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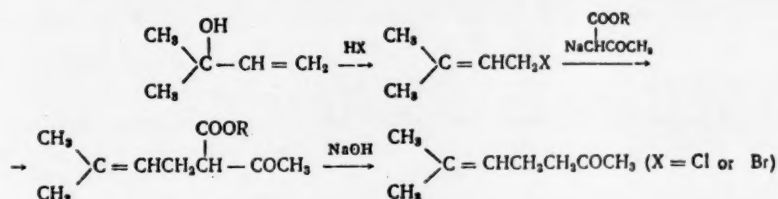
\* Original Russian pagination. See C.B. Translation.

# SYNTHESIS OF METHYLHEPTENONE AND METHYLHEPTADIENONE

Academician I. N. Nazarov, L. A. Yanovskaya, B. P. Gusev,  
S. S. Yufit, V. I. Gunar and V. A. Smit

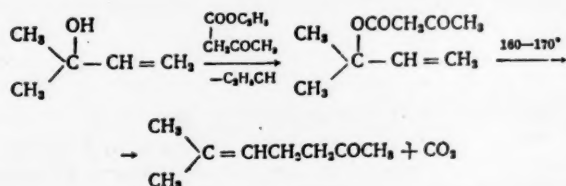
Methylheptenone and methylheptadienone are important starting substances for synthesis of natural odorous substances of the isoprenoid type (linalool, geraniol, farnesol, citral, dehydrocitral, safranal and ionone). We have made a close study of the preparation of methylheptenone starting from dimethylvinylcarbinol or isoprene and following three different routes: 1) Condensation of prenyl halides with ethyl acetoacetate [1]; 2) reaction of dimethylvinylcarbinol with ethyl acetoacetate; 3) pyrolysis of the acetoacetate of dimethylvinylcarbinol [2].

As was shown in our laboratory [3], the action of hydrogen halides on dimethylvinyl carbinol gives a high yield of the corresponding prenyl halides which readily condense with sodium ethyl acetoacetate and on subsequent saponification give methylheptenone:



All three steps of this synthesis are conveniently performed in one operation without separation of intermediate products; methylheptadienone is then obtained in 75% yield via prenyl bromide and 60% via prenyl chloride. As we know, these halides can also be prepared by the action of hydrogen halides on isoprene.

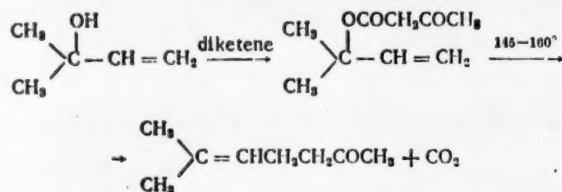
The second method of synthesis of methylheptenone consists in the direct reaction of dimethylvinylcarbinol with ethyl acetoacetate at 160-170°; it is illustrated by the following scheme:



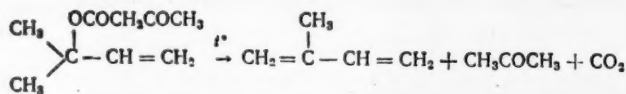
The yield of methylheptenone by this method is 60-70% ; at the same time almost the theoretical amount of ethyl alcohol and carbon dioxide is evolved. Due to the low boiling point of dimethylvinylcarbinol, this reaction must be conducted under pressure or in presence of high-boiling diluents (vaseline oil), using a high-efficiency column 100-120 cm high. If this reaction is conducted at a temperature higher than 140°, transesterification occurs and nearly the theoretical amount of ethyl alcohol distills off, but carbon dioxide is not given off, and the acetoacetate

of dimethylvinylcarbinol can be isolated by fractionation of the residue in vacuum. This ester undergoes pyrolysis at 160-170° to form methylheptenone and carbon dioxide, as illustrated by the above mechanism of the reaction. The employment of metallic sodium or other agents in this reaction is inadvisable [4].

We also made a detailed investigation of the pyrolysis of the pure acetoacetate of dimethylvinylcarbinol which is readily prepared in 90% yield by the action of diketene on dimethylvinylcarbinol in presence of a small quantity of pyridine:

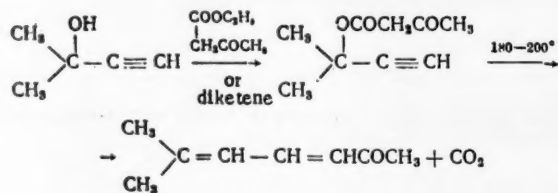


Pyrolysis of the acetoacetate of dimethylvinylcarbinol goes most smoothly without any additives at a temperature of 145-160°, methylheptenone being formed in 65-70% yield. This process in its entirety can likewise be realized in one operation without separation of the acetoacetate of dimethylvinylcarbinol in the pure form. A side reaction likewise occurs in this process with formation of isoprene, acetone and carbon dioxide:



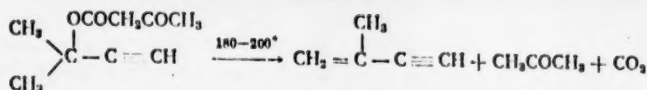
In some cases this breakdown of the acetoacetates of tertiary vinyl- and ethynylcarbinols becomes the main reaction as we established in our laboratory on a number of examples.

We also made a close study of methods of preparation of methylheptadienone both by the reaction of dimethylethynylcarbinol with ethyl acetoacetate and by pyrolysis of the pure acetoacetate of dimethylethynylcarbinol; the latter is obtained in 90% yield by the action of diketene on dimethylethynylcarbinol in presence of triethylamine:



No reaction at all takes place between dimethylethynylcarbinol and ethyl acetoacetate at below 160° (the original substances are recovered unchanged); this reaction must be conducted at 170-180°, but the yield of methylheptadienone is only about 25%.

Pyrolysis of the pure acetoacetate of dimethylethynylcarbinol in the liquid phase goes most smoothly without any added agents at a temperature of 180-200°, and methylheptadienone can be obtained in this manner in a yield of 55%. In the gas phase (in a pyrex tube), this pyrolysis takes place with appreciable velocity only at a temperature of 250-300°, and the yield of methylheptadienone is low (15-20%) even when operating in vacuum. The introduction of inert diluents and of various acids, salts and metal oxides (phosphoric and boric acids,  $\alpha$ -naphthalenesulfonic acid, copper acetate,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AlCl}_3$  etc.) did not give satisfactory results and led in some cases to complete resinification of the substance (copper acetate, boric acid,  $\text{Cu}_2\text{Cl}_2$ ). Pyrolysis of the acetoacetate of dimethylethynylcarbinol is likewise accompanied by secondary processes with formation of isopropenylacetylene and acetone:



## EXPERIMENTAL

**Preparation of methylheptenone.** a) 193 g of gaseous hydrogen bromide (3% excess) was passed into 200 g dimethylvinylcarbinol in the course of three hours while cooling with ice water (0°). The mixture was left for 2 hours at room temperature and the aqueous layer (40 ml) was separated. The bromide was washed with a solution of sodium bicarbonate and dried with calcined magnesium sulfate. 323 g of prenyl bromide was obtained and was added (without distillation) in the course of an hour to sodium ethyl acetoacetate prepared from 55 g metallic sodium and 380 g ethyl acetoacetate in 650 ml absolute alcohol. The reaction mixture was stirred for 5 hours at 5-20°, left overnight, and again stirred on the following day for 4 hours at 60°. The precipitate of sodium bromide (213 g) was filtered off, the alcohol was taken off in low vacuum, and 1100 ml 10% sodium hydroxide solution was added to the residue. The mixture was then stirred for 3 hours at 60-65°. The liquid was made acid to congo with hydrochloric acid and the product was extracted with ether, washed with bicarbonate solution, dried with magnesium sulfate and fractionated in vacuum in a column of 25 theoretical plates. 219 g (75%) of methylheptenone was obtained with b.p. 75.5-76° (25 mm),  $n_D^{20}$  1.4404. Its semicarbazone melted at 135.5-136°, the 2,4-dinitrophenylhydrazone at 85.5-86° (from aqueous alcohol).

b) 39.5 g gaseous hydrogen chloride (8% excess) was passed at 0° into 86 g dimethylvinylcarbinol in the course of 4 hours. After standing for 2 hours at room temperature, the aqueous layer (2 ml) was separated; the prenyl chloride was washed with saturated sodium bicarbonate solution, dried with magnesium sulfate and added (without distillation) by drops in the course of 2 hours to a solution of sodium ethylacetoacetate prepared from 34 g metallic sodium and 190 ml ethylacetoacetate in 300 ml absolute methanol. The mixture was stirred for 3 hours at 30-40°. The next day the precipitated sodium chloride was filtered off, the methanol was distilled off, and 600 ml of 10% sodium hydroxide solution was added to the residue; the reaction mixture was then stirred for 3 hours at 60-70°. After acidification with hydrochloric acid, the product was extracted with ether, washed with bicarbonate solution, dried with magnesium sulfate and fractionally distilled in vacuum to give 76.3 g (60%) of methylheptenone with b.p. 56-57° (9 mm) and  $n_D^{20}$  1.4403.

c) 25 ml vaseline oil was put in a flask fitted with a thermometer, a dropping funnel and a 120 cm column; slow addition by drops was then made (over a period of 6 hours) of a mixture of 43 g (0.5 mole) dimethylvinylcarbinol and 72 g (0.55 mole) ethyl acetoacetate at a temperature (in the oil) of 210°; addition was made at such a rate that the reaction mixture was maintained at not below 160-165°. Heating was then continued at 160-180° for another 3 hours (until gas ceased to come off). A total of 9 liters gas was evolved in the experiment (analysis showed a content of about 90% carbon dioxide and 10% isoprene) and 25 g distillate with b.p. up to 78° came over (ethyl alcohol with admixture of acetone). Fractionation of the residue in vacuum gave 33 g (60%) of methylheptenone with b.p. 61-62° (10 mm),  $n_D^{20}$  1.4412,  $\lambda_{\text{max}}$  243 m $\mu$  (in alcohol), log  $\epsilon$  2.54; semicarbazone, m.p. 136-137° (from alcohol).

d) To 17.2 g dimethylvinylcarbinol (0.2 mole) was added 1 ml of dry pyridine, and 21 g of 83% diketene (0.25 mole) was also added dropwise at such a rate that the temperature of the reaction mixture did not rise above 60°. After completion of the exothermic reaction, the mixture was heated at 70° for 15 min. Fractionation gave 31.4 g (92%) of the acetoacetate of dimethylvinylcarbinol with b.p. 86-88° (10 mm),  $n_D^{20}$  1.4410.

Found %: C 63.16; 63.53; H 8.19; 8.34  $\text{C}_9\text{H}_{14}\text{O}_2$ . Calculated %: C 63.51; H 8.29

Reaction of diketene with dimethylvinyl carbinol in presence of metallic sodium, as described in recent patents [2], gave the acetoacetate in a yield of only 60%.

30 g of the acetoacetate of dimethylvinylcarbinol was heated in a nitrogen atmosphere at 145-160° for 2 hours until gas ceased to come off. 2950 ml of carbon dioxide (75% of theory) was collected. Fractionation of the residue in vacuum gave 13.6 g (62%) methylheptenone with b.p. 56-58°/9mm,  $n_D^{20}$  1.4414.

Preparation of methylheptadlenone. To 84 g dimethylethynylcarbinol was added 2 ml triethylamine, and 94 g of 85% diketene was introduced by drops, while the temperature of the reaction mixture was maintained at not higher than 50°; the mixture was then heated for 30 min. at 60°. Fractionation in vacuum gave 152 g (90%) of the ethylacetoacetate of dimethylethynylcarbinol with b.p. 85-86°/10 mm,  $n_D^{20}$  1.4400. 84 g of this product was heated in a nitrogen atmosphere at 190-200° for 2 hours until gas ceased to come off. 8 liters of carbon dioxide (72% of theory) was collected. Fractionation of the residue in vacuum gave 34 g (55%) of methylheptadlenone with b.p. 77-79°/8mm,  $n_D^{20}$  1.5300. Its semicarbazone melts at 175-176° (from alcohol).

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## FERROCENE SULFONIC ACIDS

Academician A.N. Nesmeyanov, Z.G. Perevalova and S. S. Churanov

We prepared ferrocene sulfonic acids [1] by the method of A.P. Terentyev [2] (action of pyridinesulfotrioxide on ferrocene).

Our work coincided with the preparation by Weinmayr [3] of ferrocene sulfonic acids by the reaction of ferrocene with sulfuric acid in acetic anhydride; the acids were only isolated in the form of the ammonium salts.

In the present communication we describe the sulfonation of ferrocene with pyridinesulfotrioxide and dioxanesulfotrioxide, the isolation of the free mono- and disulfonic acids of ferrocene, some of their salts, the methyl esters and the acid chloride of ferrocene monosulfonic acid.

Heating of ferrocene with pyridinesulfotrioxide in dichloroethane in a sealed tube for 4 hours gives ferrocene monosulfonic acid in 84% yield, reckoned on the ferrocene going into reaction; 23% of the ferrocene is recovered unchanged. More prolonged heating of ferrocene with a larger amount of pyridinesulfotrioxide gives ferrocene disulfonic acid in 41% yield together with a small quantity of the monosulfonic acid. Only about 7% of the ferrocene is recovered unchanged. The sulfonic acids were isolated in the form of the barium or lead salts.

Free ferrocene monosulfonic acid was obtained in quantitative yield by treating the lead salt with hydrogen sulfide, as well as by sulfonation of ferrocene with dioxanesulfotrioxide at room temperature; yield 62% reckoned on the ferrocene going into reaction; 54% of the ferrocene was recovered unchanged.

Free ferrocene disulfonic acid was obtained by sulfonation with dioxanesulfotrioxide in dichloroethane, the acid being separated in the form of a complex with dioxane. (yield: 85%). Sulfonation of ferrocene with sulfuric acid in acetic anhydride [3] likewise gave the free disulfonic acid which crystallizes with 4 molecules of water. yield: 51% of the theoretical. Potentiometric titration gives a curve typical of a monobasic acid; this points to similarity between the first and second constants and consequently to the weakness of the mutual influence of the sulfo groups. This is an argument in favor of the sulfo groups being located in different rings of the ferrocene molecule.

S-Benzylthiuronium salts and salts with some amines were obtained for both sulfonic acids.

Reaction with diazomethane gave the methyl ethers of the ferrocene sulfonic acids which are soluble in organic solvents. The acid chloride of the monosulfonic acid is easily formed in good yield by brief heating of the monoacid or its lead salt with excess of  $\text{PCl}_5$ .

Ferrocene sulfonic acids differ from aromatic sulfonic acids in being less hygroscopic and more easily isolated in the free state. Noteworthy features are the fairly low solubility (for a sulfonic acid) in water of ferrocene monosulfonic acid and the facility of formation of its acid chloride by the action of  $\text{PCl}_5$  on the free sulfonic acid, which is not typical of aromatic sulfonic acids.

## EXPERIMENTAL

### Ferrocene Monosulfonic Acid

To a solution of 58 g (0.312 mole) ferrocene in 250 ml dichloroethane at 0–5° was gradually added a suspension of 55 g (0.327 mole) dioxane sulfotrioxide in 200 ml dichloroethane. The mixture was left for 30 min.

at 0-15° and for 1½ hours at room temperature; it was then treated with cold water. 31.5 g (54.3%) unreacted ferrocene was isolated from the dichloroethane solution. The aqueous solution was evaporated nearly to dryness on a water bath. The solid residue (ferrocene monosulfonic acid) was washed with 40 ml conc. HCl. Yield 13.5 g (63% reckoned on the ferrocene going into reaction). Ferrocene monosulfonic acid is poorly soluble in ether, benzene, acetone and dioxane, slightly more soluble in methyl and ethyl alcohols, rather poorly soluble in cold water. The solid monosulfonic acid contains two molecules of crystal water, as shown by the elementary analysis and determination of the equivalent weight by potentiometric titration; it decomposes when heated above 200°.

Found %: C 39.56; 39.65; H 4.38; 4.55; Fe 18.70; 18.50  $C_{10}H_{14}O_5SFe$ . Calculated %: C 39.75; H 4.69 Fe 18.49

Found equiv. weight 303; 309; calculated for  $C_{10}H_{14}O_5SFe$ : equiv. weight 302.

Free ferrocene monosulfonic acid was also obtained by treating the lead salt with hydrogen sulfide.

4 g of the lead salt was dissolved in 150 ml water. The lead was precipitated by passage of hydrogen sulfide. The precipitated PbS was separated by centrifuging. The water was taken off in vacuum in a stream of  $CO_2$ . The ferrocene monosulfonic acid was dried in a vacuum-desiccator over  $P_2O_5$ . Yield 1.5 g (97% of theory).

The same acid chloride is obtained from the ferrocene monosulfonic acid isolated from the lead salt and from the acid prepared by sulfonation of ferrocene with dioxanesulfotrioxide.

**Lead salt.** After sulfonation of ferrocene with dioxane-sulfotrioxide (conditions as described in the preceding experiment), the reaction mixture was heated with 70 g  $PbCO_3$  to give 45 g (80% reckoned on the reacted ferrocene) of lead salt of ferrocene monosulfonic acid, crystallizing from hot water with  $3H_2O$ .

Found %: C 30.10; 30.28; H 3.00; 3.05  $C_{20}H_{26}O_9S_2Fe_2Pb$ . Calculated %: C 30.34; H 3.06

**Barium salt.** A mixture of 12 g (0.065 mole) ferrocene, 40 g (0.25 mole) pyridine-sulfotrioxide and 20 ml dry dichloroethane was heated 4 hours in a sealed tube on a boiling water bath. The reaction mixture was worked up with a mixture of water and  $BaCO_3$  to give 2.7 g (22.4%) of unreacted ferrocene and 15.6 g (84% calculated on the ferrocene going into reaction) of the barium salt of ferrocene monosulfonic acid; the latter is insoluble in organic solvents, rather difficultly soluble in cold water and readily soluble in hot water; it crystallizes from water in the form of a crystal hydrate with  $3H_2O$ .

Found %: C 33.28; 33.21; H 3.44; 3.39  $C_{20}H_{24}O_9S_2Fe_2Ba$ . Calculated %: C 33.16; H 3.34

**The S-Benzylthiuronium salt** was prepared by mixing equimolar amounts of aqueous solutions of the barium salt of ferrocene monosulfonic acid and S-benzylthiuronium chloride; m.p. 220-222° (from 50% alcohol).

Found %: C 50.04; 49.91; H 4.69; 4.70  $C_{13}H_{20}O_3N_2S_2Fe$ . Calculated %: C 50.00; H 4.66

Free ferrocene monosulfonic acid forms a salt with S-benzylthiuronium chloride that is identical with the salt obtained from the barium salt.

**Salts with amines.** Ferrocene monosulfonic acid readily forms salts with aromatic and aliphatic amines which are readily soluble in water and decompose in the air. The salt with diethylamine is smoothly formed on adding excess of the amine to the sulfonic acid; m.p. 118-120°.

Found %: C 49.45; 49.52; H 6.30; 6.21; Fe 16.67; 16.60; N 4.61; 4.91  $C_{14}H_{21}O_3NSFe$ . Calculated %: C 49.56; H 6.24; Fe 16.46; N 4.13

**Methyl ether.** A suspension of 3 g ferrocene monosulfonic acid in 20 ml ether was treated with an ethereal solution of diazomethane prepared from 10.3 g nitrosomethylurea. Yield 2 g (72% of theory). M.p. 52-54° (from ether on cooling to 0°).

Found %: C 47.48; 47.39; H 4.46; 4.38; Fe 20.06; 20.05  $C_{11}H_{12}O_3SFe$ . Calculated %: C 47.16; H 4.32 Fe 19.93

**Acid chloride.** 3 g of ferrocene monosulfonic acid was added in small portions to 30 ml  $PCl_3$ . The mixture was heated 30 min. on a water bath. The solution was filtered from the small quantity of undissolved residue which was further treated with 10 ml  $PCl_3$ . The solutions were combined and part of the  $PCl_3$  (25 ml) was driven off. Dark-orange crystals of the acid chloride (0.7 g) came down on cooling. Careful addition of 25 ml cold water to the solution led to separation of another 1.05 g of acid chloride. Total yield 1.75 g (62% of theory).

The acid chloride dissolves readily in organic solvents and is slowly hydrolyzed on standing in the air with formation of the original sulfonic acid; m.p. 72-73° in an open capillary and 77-78° in a sealed capillary (from a 5:1 mixture of hexane and benzene).

Found %: C 41.89; 41.68; H 3.47; 3.60; Fe 19.70; 19.61  $C_{10}H_9O_2S_2ClFe$ . Calculated %: C 42.21; H 3.19; Fe 19.63.

The acid chloride was also obtained in good yield by similar treatment of the lead salt of ferrocene monosulfonic acid.

#### Ferrocene Disulfonic Acid

To a suspension of 10.7 g (0.0575 mole) ferrocene in 10 ml dichloroethane was added a suspension of 29 g (0.172 mole) dioxane-sulfotrioxide in 50 ml dichloroethane at a temperature of -20 to -30°. The mixture was left overnight at room temperature. The precipitated pure ferrocene disulfonic acid was filtered, washed with dioxane and dried in a vacuum-desiccator for 24 hours; it contained one molecule of crystal dioxane. Yield 21.1 g (85% of theory).

Found %: C 38.26; 38.18; H 4.40; 4.42; Fe 13.12; 13.18  $C_{14}H_{18}O_8S_2Fe$ . Calculated %: C 38.71; H 4.18; Fe 12.86

The disulfonic acid easily loses its dioxane on standing in a vacuum-desiccator and is converted into the anhydrous disulfonic acid which rapidly takes up moisture from the air.

We also obtained free ferrocene disulfonic acid by sulfonating ferrocene with sulfuric acid in acetic anhydride [3].

To a solution of 9.3 g (0.05 mole) ferrocene in 150 ml acetic anhydride was gradually added 10 ml (0.188 mole) conc. sulfuric acid with cooling to 0 to +5°. The mixture stood for 12 hours at 0°. The precipitated ferrocene disulfonic acid was filtered off, washed with a little acetic anhydride and then thoroughly washed with benzene. Yield 10.8 g (51% of theory). M.p. 80-90°; it could not be recrystallized.

Ferrocene disulfonic acid prepared by the foregoing method contains 4 molecules of crystal water as confirmed by analysis and by determination of the equivalent weight by potentiometric titration. On standing in the air the thoroughly purified acid absorbs moisture fairly slowly.

Found %: C 29.23; 29.09; H 4.58; 4.48; Fe 12.5; 12.1  $C_{10}H_{18}O_{10}S_2Fe$ . Calculated %: C 28.72; H 4.32; Fe 13.6

A purer ferrocene disulfonic acid is obtained if the product described above is extracted for a long period with benzene in a Soxhlet apparatus. After partial distillation of the benzene, golden-yellow crystals come down which are identical with those described above and give the same dimethyl ether as before, containing 4 molecules of crystal water.\*

Found %: C 28.71; 28.59; H 4.08; 4.29; Fe 13.31; 13.70  $C_{10}H_{18}O_{10}S_2Fe$ . Calculated %: C 28.72; H 4.32; Fe 13.36

Equivalent weight found 203; 203; for  $C_{10}H_{18}O_{10}S_2Fe$  equiv. weight calculated: 209.

Barium salt. 10 g (0.054 mole) ferrocene, 40 g (0.25 mole) pyridine-sulfotrioxide and 20 ml dichloroethane were heated in a sealed tube on a boiling water bath for 8 hours. After treatment of the reaction mixture with water and  $BaCO_3$ , 11.5 g (41% reckoned on the ferrocene reacted) of the barium salt of ferrocene disulfonic acid was obtained; 0.7 g (7%) of the ferrocene was recovered unchanged. The barium salt has excellent solubility in water; it is precipitated from the saturated aqueous solution by alcohol; it is freed from admixtures of the barium salt of the monosulfonic acid by repeated reprecipitation.

Found %: C 21.19; 21.22; H 2.79; 2.74  $C_{10}H_{16}O_{10}S_2FeBa$ . Calculated %: C 21.69; H 2.91

The S-benzylthiuronium salt was prepared in the same manner as the salt of the monosulfonic acid; m.p. 233-235° (from 50% alcohol or from water).

Found %: C 46.08; 46.22; H 4.74; 4.71  $C_{24}H_{30}O_6N_4S_4Fe$ . Calculated %: C 46.01; H 4.46

Salts with amines. Ferrocene disulfonic acid readily forms salts with amines when treated with excess

\* Prepared jointly with S.P. Gubin.

of the latter. The salt with dimethylaniline does not melt when heated to 250.\*

Found %: C 52.82; 52.65; H 5.52; 5.61; Fe 10.50; 10.82  $C_{16}H_{22}N_2S_2O_6Fe$ . Calculated %: C 53.09; H 5.48 Fe 10.88

Dimethyl ether. To a mixture of 0.65 g of ferrocene disulfonic acid tetrahydrate in 20 ml ether was added (ice cooling) an ethereal solution of diazomethane prepared from 5.2 nitrosomethylurea. Yield 9% of theory. M.p. 140-142°. The ether is almost insoluble in cold methyl and ethyl alcohols, acetic acid and water, poorly soluble in ether and benzene, more soluble in acetone, pyridine, dichloroethane and dioxane.

Found %: C 38.83; 38.72; H 4.19; 4.18; Fe 15.01; 14.95  $C_{11}H_{14}O_6S_2Fe$ . Calculated %: C 38.50 H 3.77; Fe 14.93

The same dimethyl ether was obtained from ferrocene disulfonic acids prepared by various methods.

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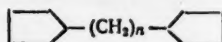
\* Prepared by S. P. Gubin.

# THE REACTION OF TETRAMETHYLENE- AND PENTAMETHYLENEDIMAGNESIUM BROMIDES WITH $\Delta^2$ -CYCLOPENTENYL CHLORIDE

A. F. Plate and V. I. Stanko

(Presented by Academician B. A. Kazansky)

In the further course of our investigations [1] on the preparation of hydrocarbons with two five-membered rings of the general formula



we have studied the preparation of 1,4-dicyclopentylbutane and 1,5-dicyclopentylpentane by the interaction of  $\Delta^2$ -cyclopentenyl chloride with dimagnesium derivatives of 1,4-dibromobutane and 1,5-dibromopentane. According to the data of Braun [2], each of these bromo derivatives gives approximately 50% of the corresponding dimagnesium derivative together with dimagnesium derivatives of products of condensation of these dibromo compounds of the general formula  $\text{BrMg}(\text{CH}_2)_n\text{MgBr}$  where  $n = 8, 12$  or  $10, 15, 20$  respectively.

It was found that the main products of reaction of  $\Delta^2$ -cyclopentenyl chloride with tetramethylene- and pentamethylenedimagnesium bromide are the expected 1,4-di( $\Delta^2$ -cyclopentenyl)-butane (47-51%) and 1,5-di( $\Delta^2$ -cyclopentenyl)-pentane (30%) respectively. In addition, however, to these hydrocarbons containing two five-membered rings, hydrocarbons with one five-membered ring were formed in both cases. The structure of the skeleton of the latter was confirmed by catalytic hydrogenation which gave, respectively, n-butylcyclopentane and n-amylicyclopentane the constants of which corresponded to the constants reported in the literature [3].

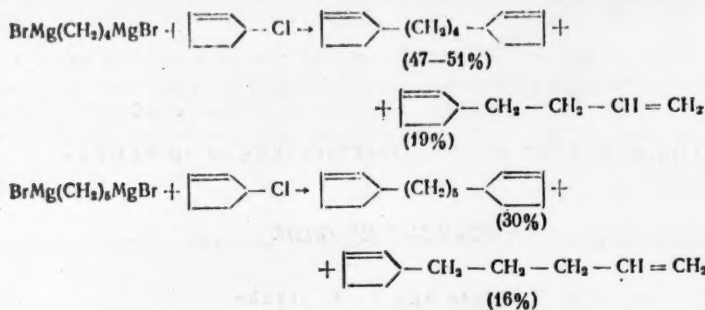
Quantitative determination of the hydrogen taken up on hydrogenation of the unsaturated hydrocarbon with one five-membered ring, obtained by reaction of  $\Delta^2$ -cyclopentenyl chloride with pentamethylenedimagnesium bromide, showed that the molecule contains two double bonds. The position of these double bonds may be established on the basis of the structure of the starting substances: one bond is evidently in position 2 of the five-membered ring in relation to the substituent, but the second bond is formed by cleavage of one molecule of hydrogen halide.

Formation of olefins under the conditions of the Grignard reaction is characteristic of secondary and tertiary alkyl halides, but this secondary reaction has also been observed in the case of primary alkyl halides. Thus, for example, Spath [4] observed the formation of ethylene and octene on reacting ethyl magnesium bromide with secondary octyl bromide, the formation of amylene on reacting isoamylmagnesium bromide with isoamyl bromide, and a number of other instances of formation of olefins in Grignard reactions.

This double bond must clearly be in the  $\alpha$ -position. Isomerization with translocation of the double bond is scarcely possible here because it is well known that reaction of alkylmagnesium halides with allyl chloride or bromide is one of the most trustworthy methods of preparation of  $\alpha$ -olefins without contamination with isomers whose double bond is in another position [5]. Consequently, the hydrocarbons obtained with one five-membered ring must clearly be assigned the structure of 1- $\Delta^2$ -cyclopentenyl)-butene-3 and 1-( $\Delta^2$ -cyclopentenyl)-pentene-4 respectively.



The results of the reactions between  $\Delta^1$ -cyclopentenyl chloride and, respectively, tetramethylenedimagnesium bromide and pentamethylenedimagnesium bromide can accordingly be represented by the following schemes:



1,4-Dicyclopentylbutane and 1,5-dicyclopentylpentane (previously unknown) were prepared by catalytic hydrogenation of 1,4-di-( $\Delta^1$ -cyclopentenyl)-butane and 1,5-di-( $\Delta^1$ -cyclopentenyl)-pentane respectively.

#### EXPERIMENTAL

**Synthesis of 1,4-dicyclopentylbutane.**  $\Delta^1$ -Cyclopentenyl chloride was obtained by addition of hydrogen chloride to cyclopentadiene [6]; it had b.p. 39-40°/45 mm and 36°/39 mm.

**1,4-Dibromobutane** was prepared [7] by the action of hydrogen bromide on 1,4-butanediol.

A Grignard reagent was made up from 216 g (1 mole) 1,4-dibromobutane and 49 g (1 g-atom) magnesium in presence of 800 ml absolute ether. 193 g (1.9 moles) of  $\Delta^1$ -cyclopentenyl chloride in 200 ml absolute ether and 5 g  $\text{Cu}_2\text{Cl}_2$  were added to the Grignard complex with cooling to -5 to 0° with ice and salt. The mass was stirred two hours at room temperature and 3 hours while heating on a water bath. After the usual treatment with water and dilute (5-10%) sulfuric acid, the ether layer was washed with water, with sodium carbonate and again with water, and dried with calcium chloride. After removal of the ether, the residue was distilled in vacuum to give two fractions: (A) with b.p. 35-85°/7 mm and (B) with b.p. 107-110°/7 mm.

Fractionation of A in a column \* gave 23 g 1-( $\Delta^1$ -cyclopentenyl)-butene-3 (yield 19% of theory) with the following constants: b.p. 150°/749 mm;  $n_D^{20}$  1.4492;  $d_4^{20}$  0.8120; found  $\text{MR}_D$  40.31; calculated for  $\text{C}_9\text{H}_{14}$  2F  $\text{MR}_D$  40.62.

The hydrocarbon skeleton of 1-( $\Delta^1$ -cyclopentenyl)-butene-3 was confirmed by hydrogenation of 10 g in the cold in solution in 15 ml alcohol in presence of skeletal nickel \*\* under a hydrogen pressure of 75-80 atm. The hydrocarbon was washed free from alcohol and dried over calcium chloride; it was purified by chromatographic adsorption over 6 g silica gel. Fractionation in a column gave n-butylcyclopentane with the following constants: b.p. 155.5°/750 mm;  $n_D^{20}$  1.4320;  $d_4^{20}$  0.7836; the literature [3] reports: b.p. 155.56°/760 mm;  $n_D^{20}$  1.4316;  $d_4^{20}$  0.7846.

99 g of fraction B was isolated from the products of interaction of  $\Delta^1$ -cyclopentenyl chloride with tetramethylenedimagnesium bromide; it was distilled in a column to give 88 g of 1,4-di-( $\Delta^1$ -cyclopentenyl)-butane (yield 51% of theory) \*\*\* with the following constants: b.p. 120.5°/7.5-8 mm;  $n_D^{20}$  1.4838;  $d_4^{20}$  0.8849; found  $\text{MR}_D$  61.46; calculated for  $\text{C}_{14}\text{H}_{22}$  2F  $\text{MR}_D$  61.52.

88 g of 1,4-di-( $\Delta^1$ -cyclopentenyl)-butane was hydrogenated in the cold in solution in 60 ml acetone in presence of 15 g skeletal nickel at a pressure of 75-80 atm. The acetone was washed with water; the hydrocarbon was dried with calcium chloride, subjected to chromatographic adsorption on 100 g silica gel and fractionated in a column. After a second chromatographic adsorption, the 1,4-dicyclopentylbutane had the

\* A column with an efficiency of 40-45 theoretical plates was employed here and subsequently. The column was charged with copper packing elements.

\*\* The catalyst was prepared by leaching out 50% of the aluminum from a 1:1 aluminum-nickel alloy.

\*\*\* In the absence of  $\text{Cu}_2\text{Cl}_2$  the yield of 1,4-di-( $\Delta^1$ -cyclopentenyl)-butane was 47%.



following constants: b.p. 108°/2.5-3 mm;  $n_D^{20}$  1.46727;  $d_4^{20}$  0.8603; found  $MR_D$  62.56; calculated for  $C_{14}H_{26}$   $MR_D$  62.48.

Found %: C 86.75; 86.85; H 13.34; 13.45  $C_{14}H_{26}$ . Calculated %: C 86.60; H 13.40

**Synthesis of 1,5-dicyclopentylpentane.** 1,5-Dibromopentane was prepared from 240 g benzoylpiperidine [8]; the latter was obtained by benzylation of piperidine [9]. During the synthesis benzonitrile is formed side by side with 1,5-dibromopentane and interferes with the reaction with magnesium [2] even when present to the extent of only 1%. The 1,5-dibromopentane was therefore fractionated in vacuum in a glass-packed column with an efficiency of 15 theoretical plates. From 140 g of crude 1,5-dibromopentane was obtained 102 g of product with the following constants: b.p. 112°/25 mm;  $n_D^{20}$  1.5139;  $d_4^{20}$  1.6985; literature data [10]: b.p. 95.5°/10 mm;  $n_D^{20}$  1.5136;  $d_4^{20}$  1.6995.

The procedure for preparation of 1,5-di-( $\Delta^2$ -cyclopentenyl)-pentane was the same as that described for the synthesis of 1,4-( $\Delta^2$ -cyclopentenyl)-butane, starting from 102 g (0.45 mole) 1,5-dibromopentane, 24.5 g (1 g-atom) magnesium and 91 g (0.9 mole)  $\Delta^2$ -cyclopentenyl chloride, without addition of  $Cu_2Cl_2$ . The ether was driven off and the product was separated into two fractions: A with b.p. 84-142°/25 mm and B with b.p. 142-164°/20-25 mm.

Fraction A (22 g) was distilled in a column to give 11 g of 1-( $\Delta^2$ -cyclopentenyl)-pentene-4 (yield 16% of theory) with the following constants: b.p. 173°/745 mm;  $n_D^{20}$  1.4561;  $d_4^{20}$  0.8186; found  $MR_D$  45.6; calculated for  $C_{10}H_{16}$  2F  $MR_D$  45.24.

For confirmation of the presence of two double bonds in 1-( $\Delta^2$ -cyclopentenyl)-pentene-4, 1.104 g of the hydrocarbon was hydrogenated in the cold in presence of 0.1 g platinum black. In this operation 399 ml hydrogen was absorbed at 744 mm and 19° or 362 ml under normal conditions. The theoretically necessary amount of hydrogen for saturation of two double bonds is 364 ml.

Confirmation of the hydrocarbon skeleton of this hydrocarbon was obtained by hydrogenating another portion (6 g) of 1-( $\Delta^2$ -cyclopentenyl)-pentene-4 in the cold in solution in 25 ml alcohol in presence of 5 g skeletal nickel at a pressure of 75-80 atm. The separated hydrocarbon was chromatogrammed on 5 g silica gel, after which 5 g of the product was distilled in a column to give 3 g of n-amylicyclopentane with the following properties: b.p. 179°/749 mm;  $n_D^{20}$  1.4360;  $d_4^{20}$  0.7921. Literature data [3]: b.p. 180°/760 mm;  $n_D^{20}$  1.4358;  $d_4^{20}$  0.7912.

Fraction B (45 g) was likewise fractionated in a column and gave 27 g of 1,5-di-( $\Delta^2$ -cyclopentenyl)-pentane (yield 30% of theory) with the following constants: b.p. 151.5°/12 mm;  $n_D^{20}$  1.4849;  $d_4^{20}$  0.8920; found  $MR_D$  65.63; calculated for  $C_{15}H_{24}$  2F  $MR_D$  65.93.

27 g of 1,5-di-( $\Delta^2$ -cyclopentenyl)-pentane was hydrogenated in the cold in presence of 15 g skeletal nickel in solution in 50 ml acetone at a pressure of 75-80 atm. The resultant 1,5-dicyclopentylpentane was purified in the same way as 1,4-dicyclopentylbutane, and a preparation with the following constants was obtained: b.p. 154.0-154.5°/12-12.5 mm;  $n_D^{20}$  1.46816;  $d_4^{20}$  0.8604; found  $MR_D$  67.18; calculated for  $C_{15}H_{28}$   $MR_D$  67.07.

Analysis:

Found %: C 86.35; 86.21; H 13.51; 13.52  $C_{15}H_{28}$ . Calculated %: C 86.54; H 13.46

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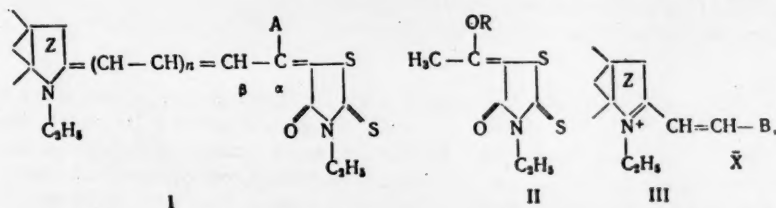
# MEROCYANINE DYES WITH ELECTRON-DONATING SUBSTITUENTS IN THE POLYMETHINE CHAIN

Z. P. Sytnik, L. D. Zhilina and E. B. Lifshits

(Presented by Academician L. L. Knunyants, January 12, 1957)

Of the chain-substituted merocyanine dyes [1-4], the only members to have been adequately investigated are the dimethinemerocyanines—derivatives of rhodanine with an alkyl or phenyl group in the polymethine chromophore [1,4a].

It was consequently of interest to study methods of synthesis and properties of di- and tetramethinemerocyanines containing an electropositive substituent in the  $\alpha$ -position, for example an alkoxy, amino or substituted amino group (I).



where Z = a heterocyclic residue; A = OR, NH<sub>2</sub>, NHR', NC<sub>2</sub>H<sub>5</sub> or NR'COCH<sub>3</sub>; R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>; R' = H, alkyl, benzyl or phenyl; B = OCH<sub>3</sub>, SCH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>NC(=O)CH<sub>3</sub>; n = 0 or 1;  $\bar{X}$  = an acid radical.

Reaction of 3-ethyl-5-( $\alpha$ -ethoxyethylidene)-rhodanine [5] (II, R = C<sub>2</sub>H<sub>5</sub>) with the ethyl p-toluenesulfonate of 2-ethylmercaptobenzothiazole in an alcoholic medium in presence of triethylamine at the ordinary temperature gave  $\alpha$ -ethoxydimethinemerocyanine (I, A = OC<sub>2</sub>H<sub>5</sub>, n = 0, Z = the benzothiazole residue; bright-red needles with m.p. 154°).

Found %: N 7.09; 7.06 C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>S<sub>3</sub> Calculated %: N 7.13 (compare [2a])

$\alpha$ -Ethoxy-substituted dimethinemerocyanines containing the following residues were similarly synthesized: 6,7-tetramethylenebenzothiazole, benzoselenazole, quinoline (2), benzoxazole and thiazoline; in the case of derivatives of benzoxazole and thiazoline, the reaction was performed in a medium of acetic anhydride in presence of triethylamine and with heating.

Subsequently we effected the preparation of  $\alpha$ -ethoxytetramethinemerocyanines (I, A = OC<sub>2</sub>H<sub>5</sub>, n = 1) containing the benzothiazole residue (dark-blue, lustrous needles with m.p. 160°).

Found %: N 6.51 C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>N<sub>2</sub>S<sub>3</sub> Calculated %: N 6.69 [11]

Similarly we prepared the same type of compound containing the benzoselenazole or the 3,3-dimethylindolenine residue. These syntheses were realized by condensation of 3-ethyl-5-( $\alpha$ -ethoxyethylidene)-rhodanine (II, R = C<sub>2</sub>H<sub>5</sub>) with quaternary salts of vinyl derivatives of heterocyclic bases containing an easily split-off group III, in solution in ethyl alcohol or acetic anhydride in presence of triethylamine.

It was to be expected that in these dyes (I, A = OR) the alkoxy group, just as in 3-ethyl-5-( $\alpha$ -ethoxyethylidene)-rhodanine [5], see also [6-8], would be extremely labile and would in particular be capable of exchanging with an amine radical and so enable us to pass from these compounds to the previously undescribed  $\alpha$ -amino-substituted merocyanines.

In fact, after heating for 1 hour  $\alpha$ -ethoxy- or  $\alpha$ -methoxydimethinemerocyanine (a benzothiazole derivative) with excess of ethylamine (30 moles per mole of dye) in alcoholic solution, the color of the latter was appreciably intensified. In both cases good yields were obtained of dyes with identical properties; their elementary composition showed that they were merocyanine with an ethylamino group in the  $\alpha$ -position (light yellow needles with m.p. 167°).

Found %: N 10.52  $C_{18}H_{21}ON_3S_3$  Calculated %: N 10.70

The reaction went in exactly the same direction with methyl-, butyl-, n-nonyl-, n-dodecyl- and benzylamines.

Syntheses were realized in a completely analogous manner (by the action of ethylamine on the corresponding  $\alpha$ -ethoxymmerocyanines) of the  $\alpha$ -ethylamino-substituted dimethinemerocyanines containing the 6,7-tetramethylene-benzothiazole, benzoselenazole, quinoline (2) and thiazoline residues; likewise a tetramethinemerocyanine (I, A =  $NHC_2H_5$ , n = 1) — a benzothiazole derivative (dark-red needles with m.p. 146°).

Found %: N 9.84  $C_{20}H_{23}ON_3S_3$ . Calculated %: N 10.06

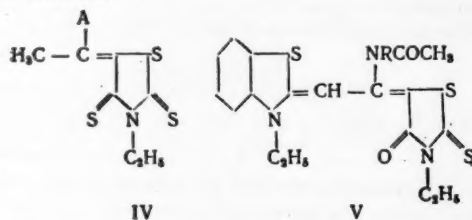
Exchange of the ethoxy or methoxy group in merocyanines of structure I (A = OR) also takes place at the ordinary temperature but very much more slowly. Under these conditions we reacted an  $\alpha$ -ethoxymmerocyanine (benzothiazole derivative) with ammonia in alcoholic solution for 15 days and obtained an  $\alpha$ -amino-substituted dye (I, A =  $NH_2$ , n = 0; orange prisms with m.p. 227°).

Found %: N 11.57  $C_{16}H_{17}ON_3S_3$ . Calculated %: N 11.56

Heating in this case leads to a series of secondary reactions.

The reaction of  $\alpha$ -ethoxydimethinemerocyanine (a benzothiazole derivative) with aniline and secondary amines goes quite differently. Heating with 30 moles piperidine without a solvent at 100° or in boiling ethyl alcohol led only to traces of an  $\alpha$ -N-piperidyl-substituted dye; the main product of the reaction was a yellow substance (m.p. 198°, absorption maximum at  $\lambda$  441 m $\mu$ ) which differed from merocyanines in being firmly adsorbed on alumina and in being difficultly soluble in nonpolar solvents. A dye with a piperidine residue in the  $\alpha$ -position was obtained in small yield by heating  $\alpha$ -methylmercaptodimethinemerocyanine with piperidine at 100°.

Substitution of both the ethoxy- and the methylmercapto group with aniline and diethylamine could not be realized under the above conditions.



where A =  $NH_2$ ,  $NHCH_3$ ,  $NHC_2H_5$ ,  $NHC_6H_5$  or  $NC_2H_5$ ; R = H,  $C_2H_5$  or  $C_6H_5$

It was also found that 3-ethyl-5-( $\alpha$ -ethoxyethylidene)-rhodanine (II, R =  $C_2H_5$ ) reacts with aniline and piperidine just as easily as with ammonia and primary aliphatic amines (for example with methyl- or ethylamine) [5a] with formation of amino-substituted ethylidenerhodanines (IV).

As in the case of quaternary salts of  $\beta$ -alkoxypropenyl derivatives of heterocyclic bases [6], the substitution of the ethoxy group in  $\alpha$ -ethoxyethylidenerhodanine (II, R =  $C_2H_5$ ) by the radical of an aliphatic amine leads to a marked fall in reactivity of the methyl group in these compounds. This phenomenon is manifested to an appreciably lesser degree, however, in the case of 3-ethyl-5-( $\alpha$ -phenylaminoethylidene)-rhodanine (IV, A =  $NHC_6H_5$ ). Condensation of the latter with the ethyl p-toluenesulfonate of 2-ethylmercaptobenzothiazole enabled

us to obtain an  $\alpha$ -phenylaminodimethinemerocyanine containing the benzothiazole residue (I,  $n = 0$  A =  $\text{NHC}_6\text{H}_5$ ).

As was expected, acetylation of the amino group in compound IV leads to appreciable lowering of the mobility of the hydrogen atoms of the methyl group. Thus, heating of 3-ethyl-5-( $\alpha$ -aminoethylidene)-rhodanine (IV, A =  $\text{NH}_2$ ) with the ethyl *p*-toluenesulfonate of 2-ethylmercaptobenzothiazole in a mixture of pyridine and acetic anhydride in presence of triethylamine leads to a dimethinemerocyanine containing the acetamino group in the  $\alpha$ -position (V, R = H; dark-red prisms with m.p. 236°).

Found %: N 10.31  $\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}_3\text{S}_3$ . Calculated %: N 10.36

Similarly, starting from the corresponding ethylidenerhodanines (IV, A =  $\text{NHC}_2\text{H}_5$  or  $\text{NHC}_6\text{H}_5$ ) we synthesized  $\alpha$ -ethylacetamino- and  $\alpha$ -phenylacetaminomerocyanines (V, R =  $\text{C}_2\text{H}_5$  or  $\text{C}_6\text{H}_5$ ). We also showed that dyes of the structure V can likewise be obtained by acetylation of the respective  $\alpha$ -amino-,  $\alpha$ -ethylamino- and  $\alpha$ -phenylaminomerocyanines.

The absorption maxima of the synthesized di- and tetramethinemerocyanines (I) containing the benzothiazole residue, as well as the maxima of some other dyes of this group are listed in Table 1 (in ethyl alcohol).

TABLE 1

A	$\lambda_{\text{max}}$ in $\mu$	Shift of absorption maximum in $\mu$
$n = 0$		
H	524 <sup>(*)</sup>	—
$\text{C}_6\text{H}_5$	536 <sup>(*)</sup>	+ 12
$\text{CH}_3\text{O}$	519	— 5
$\text{C}_2\text{H}_5\text{O}$	521	— 3
$\text{NH}_2$	467	— 57
$\text{CH}_3\text{NH}$	452	— 72
$\text{C}_2\text{H}_5\text{NH}$	454	— 70
$n\text{-C}_4\text{H}_9\text{NH}$	453	— 71
$n\text{-C}_6\text{H}_{13}\text{NH}$	451	— 73
$n\text{-C}_{12}\text{H}_{25}\text{NH}$	452	— 72
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}$	455	— 69
$\text{C}_6\text{H}_5\text{NH}$	499	— 25
$\text{C}_6\text{H}_{10}\text{N}$	471	— 51
$\text{NHCOCH}_3$	542	+ 18
$\text{C}_6\text{H}_5\text{NCOCH}_3$	541	+ 17
$\text{C}_6\text{H}_5\text{NCOCH}_3$	545	+ 21
$n = 1$		
H	607 <sup>(*)</sup>	—
$\text{CH}_3\text{O}$	607	0
$\text{C}_2\text{H}_5\text{O}$	607	0
$\text{C}_6\text{H}_5\text{NH}$	520	— 87

As was previously observed [1], the introduction of a weakly electropositive ethyl group into the  $\alpha$ -position of the polymethine chain causes a shift of the absorption maximum towards the long-wave region. Progressive intensification of the electron-donating character of the substituent (A) is accompanied (see Table 1) by a hypsochromic shift which is particularly marked with the alkylamino-substituted derivatives (69–73  $\mu$ ); the shift is appreciably larger in the case of tetramethinemerocyanine ( $n = 1$ , 87  $\mu$ ).

A similar change of position of the absorption maximum on introduction of alkoxy and ethylamino groups occurs also with merocyanines containing the residues of 6,7-tetramethylenebenzothiazole, benzeneselenazole, quinoline (2) and thiazoline.

The deepening of the color on introduction of strongly electronegative substituents into the  $\alpha$ -position of merocyanines is evidently accounted for by migration of electrons from these groups to the carbonyl oxygen of the rhodanine residue. The resultant formation of a new positively charged center and the consequent upsetting of the uniformity of distribution of the electronic density in the main chromophoric system leads, just as in the case of thiocarbocyanine [8] and triphenylmethane [10] dyes, to a heightening of the color.

In accordance with the above observations, the acetylation of the amino group results in a sharp bathochromic shift of the absorption maximum of the dyes (Table 1); the acetyl group attracts electrons from the nitrogen atom of the amino group and thereby decreases the extent of the electronic migration from this substituent to the carbonyl oxygen of the rhodanine residue.

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## THE KINETICS OF LIQUID-PHASE HYDROBROMINATION OF ACETYLENE IN PRESENCE OF MERCURY SALTS

R. M. Flid and V. A. Mironov

(Presented by Academician I. N. Nazarov, December 14, 1956)

Very few investigations have been reported [1,2] on the liquid phase catalytic interaction of acetylene with hydrogen halides in presence of mercury salts. These reactions have usually been examined under flow conditions.

Hydrobromination of acetylene in presence of mercury salts has only been studied in the vapor phase. It is reported that, apart from vinyl bromide, various isomers of dibromoethane or their mixtures are formed [3], whereas in hydrochlorination and hydroiodination under similar conditions the only dihalo derivatives identified were the asymmetric isomers. We were prompted to make a detailed study of the liquid phase hydrobromination in connection with the possibility of obtaining both of the isomers of dibromoethane.

Investigations were carried out in an apparatus permitting continuous introduction of exactly proportioned volumes of thoroughly purified acetylene and hydrogen bromide via a Schott filter into a reactor filled with the catalyst solution. The latter was a solution of mercuric bromide in hydrobromic acid whose concentration corresponded to the limiting saturation at the working temperature \*.

The dibromoethane and vinyl bromide in the vapor/gas mixture coming from the reactor were consecutively condensed in a water condenser and in traps cooled with dry ice and acetone. Unreacted hydrogen bromide was absorbed by a known excess of standard caustic alkali; unchanged acetylene was collected in a special vacuum gasholder.

All the experiments were performed at a temperature of  $100 \pm 0.5^\circ$  and in a vacuum of 90-100 mm mercury which ensured complete removal of the products of reaction from the catalyst solution when the process was run under static conditions. The volume of catalyst solution in all experiments was 175 ml.

Fractionation of the high-boiling condensates (washed with sodium carbonate solution and water) from all the sets of acetylene hydrobromination experiments confirmed the formation in this process of pure 1,1-dibromoethane (b.p.  $107-108.5^\circ$ )  $n_D^{20}$  1.5126) in addition to vinyl bromide.

**A. Influence of ratio of reactants on the degree of conversion of acetylene.** The catalyst solution used in this set of experiments had a  $HgBr_2$  concentration of 200 g/100; the molar ratio of  $HBr$  to  $C_2H_2$  was varied in the range of 0.5-4 at a constant overall space velocity of the reactants of  $5.82 \pm 0.18$  normal liters/hour, corresponding to a contact time ( $\tau$ ) of  $37.25 \pm 1.1$  sec.

It was established that both the total degree of conversion of acetylene and the yield of vinyl bromide and ethyldene dibromide does not depend upon the ratio of reactants within the limits specified above. This observation clearly indicates that the reaction is of zero kinetic order with respect to hydrogen bromide.

**B. Influence of contact period on the velocity of hydrobromination of acetylene.** Experiments were performed with a catalyst solution of the above composition at constant  $HBr/C_2H_2$  ratio of close on 1:1. The overall space velocity of the reactants was varied in the range of 2-20 normal liters/hour, corresponding to a contact period of 200-20 sec. Results of the experiments are plotted in Fig. 1. The relatively small change

\* Due to the slight change of concentration of  $HBr$  in the catalyst solution after  $HgBr_2$  had been dissolved by heating to the experimental temperature, the composition of the catalyst solution is characterized in the further course of the paper by the number of grams of  $HgBr_2$  per 100 g water (g/100).

in degree of conversion of acetylene ( $\alpha_0$ ) as a function of  $\tau$  is noteworthy (a tenfold increase of the latter corresponds to only an approximately threefold increase in yield of reaction products). This may be associated with considerable inhibition of the reaction by its products.

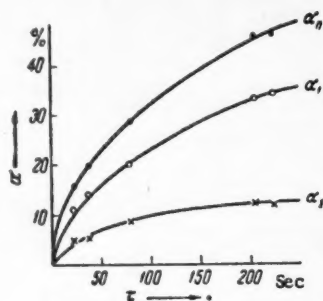
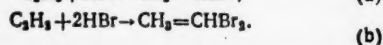
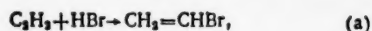


Fig. 1.

Analysis of the experimental data shows that the ratio of yields of reaction products [vinyl bromide ( $\alpha_1$ ) and ethylidene dibromide ( $\alpha_2$ )] does not depend upon  $\tau$  but fluctuates round the value

$$n = \frac{\alpha_1}{\alpha_2} = 2.61 \quad (1)$$

to an accuracy of  $\pm 0.3$ , and this can only be due to the occurrence of two independent parallel reactions obeying identical kinetic equations:



If this hypothesis is correct, the following equations should be valid:

$$K_0 = K_1 + K_2, \quad (2)$$

$$\frac{K_1}{K_2} = \frac{\alpha_1}{\alpha_2} = n = \text{const}, \quad (3)$$

where  $K_0$ ,  $K_1$ , and  $K_2$  are the velocity constants of the overall conversion of acetylene, of the formation of vinyl bromide and of the formation of ethylidene dibromide respectively.

The only kinetic equations that satisfy the experimental data were found to be equations that we derived on the assumption that both of the parallel reactions (each first-order with respect to acetylene) are inhibited by both of the reaction products, the degree of inhibition being unity. In the general form, these equations (when differentiated) will have the form:

$$\frac{d\alpha_i}{d\tau} = K_i \frac{1 - \alpha_0}{\alpha_0}. \quad (4)$$

From the relation  $\alpha_0 = \alpha_1 + \alpha_2$  and the equality (1) we obtain:

$$\alpha_0 = S\alpha_1 = (n+1)\alpha_2 \quad \text{и} \quad \alpha_1 = n\alpha_2, \quad (5)$$

where the operator  $S$  has the value

$$S = \frac{n+1}{n} = \text{const} = 1.382. \quad (6)$$

By appropriate substitutions and by integration we obtain the following expressions:

a) for the overall conversion of acetylene:

$$K_0 = \frac{1}{\tau} \left( \ln \frac{1}{1 - \alpha_0} - \alpha_0 \right); \quad (7)$$

b) for formation of vinylbromide:

$$K_1 = \frac{1}{\tau} \left( \frac{1}{S} \ln \frac{1}{1 - S\alpha_1} - \alpha_1 \right); \quad (7^1)$$

c) for formation of ethylidene dibromide:

$$K_2 = \frac{1}{\tau} \left( \frac{1}{n+1} \ln \frac{1}{1 - (n+1)\alpha_2} - \alpha_2 \right). \quad (7^2)$$

Experimental values of  $\alpha_1$  and values of  $K_1$  calculated from equations (7) are presented in Table 1.

TABLE 1

No	$\tau$ , sec.	$\alpha_1$ , %	$\alpha_2$ , %	$\alpha_3$ , %	n	$K_1 \cdot 10^4$	$K_2 \cdot 10^4$	$K_3 \cdot 10^4$
1	21.75	16.05	11.1	4.95	2.25	7.26	5.24	1.582
2	37.25	19.21	14.2	5.01	2.83	6.35	5.10	2.34
3	79.9	28.75	20.0	8.75	2.29	6.82	5.32	2.13
4	206.0	45.6	33.3	12.3	2.71	7.72	5.68	1.09
5	224.0	46.15	34.6	11.55	2.98	7.25	5.67	1.558
Mean . . .					2.61	7.08	5.42	1.92

The adequate constancy of  $K_1$ , the mean values of which satisfy the conditions of (1) ( $K_1 + K_2 = 7.34 \cdot 10^{-4}$ ,  $K_1/K_2 = 2.82$ ), confirms the validity of the above assumptions.

The kinetic measurements thus reveal the following: 1) the formation of 1,1-dibromoethane in the hydrobromination of acetylene is the result of direct simultaneous addition of two molecules of HBr to  $C_2H_2$  without participation of vinyl bromide as intermediate product, i.e. vinyl bromide and ethylidene dibromide are formed by two independent, parallel reactions; 2) both of the parallel reactions are first-order with respect to acetylene and are inhibited by both of the products of the reaction.

Further confirmation that the two reactions proceed in parallel is forthcoming by direct experimental evidence - the formation of the other isomeric dibromoethane by reaction of vinyl bromide with HBr. Hydrobromination of vinyl bromide under analogous conditions goes very much more slowly than the hydrobromination of acetylene (degree of conversion of vinyl bromide 8-10%, compared with a degree of conversion of acetylene of 30-35%), and the dibromo product is nearly pure 1,2-dibromoethane (b.p. 126.5-130°,  $n_D^{25}$  1.5340).

**C. Influence of concentration of mercuric bromide in the catalyst solution on the rate of hydrobromination of acetylene.** This set of experiments was performed with constant overall space velocity of reactants of  $6.05 \pm 0.42$  normal liters / hour on entry into the reaction column using a ratio of HBr to  $C_2H_2$  of approximately 1:1. Four different catalyst solutions were used and had  $HgBr_2$  contents of 60, 150, 275 and 400g/100. Measurements were made in  $1 \frac{1}{2}$  - 2 hours after the initial 15-minutes passage of a mixture of nitrogen and HBr at the specified velocity with the objective of attaining an equilibrium concentration of HBr in the catalyst solution.

As we see from Table 2,  $\alpha_0$  rises monotonically with increasing concentration of  $HgBr_2$ ;  $\alpha_1$  passes through a maximum;  $\alpha_2$  rises fairly steeply.

TABLE 2

No	$C_{HgBr_2}$	$\alpha_0$ , %	$\alpha_1$ , %	$\alpha_2$ , %	$\tau$ , sec.	$K_1 \cdot 10^4$	$K_2 \cdot 10^4$	$K_3 \cdot 10^4$	$lg(K_1 \cdot 10^4)$	$lg(K_2 \cdot 10^4)$	$lg(K_3 \cdot 10^4)$	$\alpha_0$	$\frac{HBr}{HgBr_2}$
1	60	7.6	7.58	0	74.3	7.0	0	0.845	0.845	—	0.4035	10.80	
2	150	27.7	25.4	2.3	83.5	43.8	40	3.8	1.641	1.642	0.580	4.21	
3	275	35.4	21.4	12.0	90.5	70.7	24.0	1.845	1.669	1.380	0.5414	2.25	
4	400	41.8	20.7	21.0	97.1	134.0	66.2	67.8	2.127	1.821	1.831	0.5514	1.489

This fact may be interpreted as an increased probability of a triple collision of a molecule of acetylene with two molecules of catalyst when the concentration of  $\text{HgBr}_2$  is increased. In solution in hydrobromic acid it is known that  $\text{HgBr}_2$  forms the stable complex anions:  $\text{HgBr}_3^-$  and  $\text{HgBr}_4^{2-}$ . Our calculated molar ratios of  $\text{HBr}$  to  $\text{HgBr}_2$  (Table 2) for the various catalyst solutions show convincingly that substantially all of the mercury in the solution is present only in complex form and that with rising concentration of  $\text{HgBr}_2$  in the catalyst solution the concentration of  $\text{HgBr}_3^-$  increases.

There are two reasons for assuming that the latter ion catalyzes the reaction. The  $\text{HgBr}_4^{2-}$  ion is coordinatively saturated and is therefore unlikely to participate in the activation of acetylene. Secondly, its concentration falls with increasing concentration of  $\text{HgBr}_2$  in the solution due to increase in the  $\text{HgBr}_2$ :  $\text{HBr}$  ratio.

On the basis of kinetic equations (7) the velocity constants  $K_0$ ,  $K_1$  and  $K_2$  were calculated for all of the four concentrations of catalyst; the values of each of them rises with increasing concentration of  $\text{HgBr}_2$ ; that of  $K_2$  rises faster than that of  $K_1$  (see Table 2).

We put forward the hypothesis that the activation of acetylene involves capture by the catalyst of a  $\pi$ -electron doublet. If the rate-determining step in hydrobromination of acetylene is the activation of the latter, we should expect to find a correlation between the oxidation potential of the catalyst solution (as a measure of its acceptor ability) and its catalytic activity. Oxidation potentials of the catalyst solutions ( $\epsilon$ ) were measured at  $t = 95 \pm 0.1^\circ$  by the procedure described by one of the authors [4].

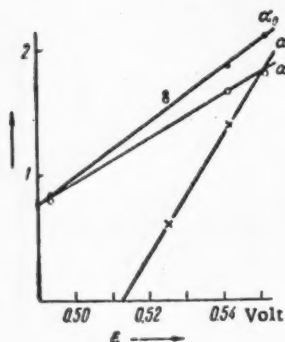


Fig. 2

As shown in Fig. 2, the linear relation between  $\log K$  and  $\epsilon$  is maintained for both of the hydrobromination reactions and for the overall acetylene conversion, the sole possible cause of the rise of the velocity of the reactions with increasing magnitude of  $\epsilon$  being the fall in activation energy. The linearity of the function  $\log K = \varphi(\epsilon)$  confirms that the activation of acetylene is the rate determining step in hydrobromination.

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## THE CATALYTIC DEHYDROGENATION OF CYCLOPENTENE

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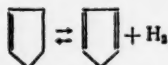
Only a few papers have been published on the transformations of cyclopentene under conditions of dehydrogenation catalysis. Thus, Plate [1,2] passed cyclopentene at 450-500° over oxides of vanadium and chromium deposited on alumina and observed partial dehydrogenation of the cyclopentene to cyclopentadiene and simultaneous hydrogenation to cyclopentane.

Still earlier, Zelinsky and Arbuzov [3] had shown that cyclopentene is perfectly stable in contact with alumina and chromium oxide at 450°. Greenfelder and Voge [4] found that in presence of zirconium aluminosilicate at 500°, cyclopentene is transformed mainly into aromatic hydrocarbons.

Vanas and Walters [5] studied the thermal breakdown of cyclopentene in a static system at 438-548° and a pressure of 38-244 mm; they showed that the main reaction under their chosen conditions is dehydrogenation, although the degree of conversion of cyclopentene did not exceed 25%.

In a number of investigations [6-10] it was shown that cyclopentadiene can be obtained directly by dehydrogenation of cyclopentane, but the yields of cyclopentadiene under these conditions did not exceed 3-11%.

Our objective in the present work was to establish the conditions for maximum conversion of cyclopentene into cyclopentadiene. It was found that at 600°, in presence of the aluminum-chromium-potash catalyst described by one of us [11], cyclopentadiene can be obtained in a yield of up to 58%. Since the dehydrogenation of cyclopentene to cyclopentadiene is accompanied by an increase in volume, a fall in pressure is therefore



bound to shift the equilibrium from left to right; the reaction was accordingly carried out at reduced pressure (20 mm).

Cyclopentene was prepared by dehydration of cyclopentanol over anhydrous magnesium sulfate at 310-315°; it had the following constants: b.p. 44.5°/758 mm;  $d_4^{20}$  0.7714;  $n_D^{20}$  1.4220;  $MR_D$  found 22.36;  $MR_D$  calculated for  $C_5H_8$ , 22.62.

Dehydrogenation was conducted in a flow system in presence of a catalyst consisting of oxides of aluminum, chromium and potassium with a molar ratio of components of 42:7:1. 50 ml (38.6 g) cyclopentene was taken in each experiment and was passed over the catalyst with a velocity of 1.0 hour<sup>-1</sup>.

The catalyzates, after determination of their content of cyclopentadiene by Afanasyev's method [12], were subjected to close fractionation in a column with an efficiency of 70 theoretical plates. The isolated fractions were analyzed by optical and chemical methods, and the composition of the gaseous products, collected in liquid nitrogen-cooled traps, was determined first in the Orsat-Lunge apparatus and then in more detail by the chromatographic method [13]. The butadiene content of the gas was determined in the Korotkov apparatus [14].



Results of the experiments on dehydrogenation of cyclopentene are set forth in Table 1. They show that with rising temperature (from 500 to 650°) the content of cyclopentadiene in the catalyzate increases, but the maximum yield of cyclopentadiene (59% calculated on the cyclopentene taken) was obtained at 600°. The composition and properties of fractions of the combined catalyzate are given in Table 2; the fractionation curve is plotted in Fig. 1. 120 g of the substance was taken for fractionation. The data of Table 2 indicate that the catalyzate consists mainly of cyclopentadiene (the adduct with maleic anhydride melted at 161° [8] together with a small amount of unchanged cyclopentene and a residue.

TABLE 1

Temperature in °C	Yield of catalyzate		Properties of catalyzate		Content of cyclopentadiene in catalyzate in %	% yield cyclopentadiene calc. on cyclopentene taken	% coke formation
	g	%	$n_D^{20}$	$d_4^{20}$			
500	31.9	82.4	1.4410	0.8015	55	45	8
	32.4	83.6	1.4412	0.8019	53	44	7
550	31.1	80.5	1.4440	0.8039	69	56	8
	29.8	76.9	1.4452	0.8047	70	54	8
600	29.5	76.1	1.4465	0.8085	76	58	10
	28.7	74.1	1.4462	0.8095	74	55	11
650	26.3	68.5	1.4470	0.8090	77	53	13

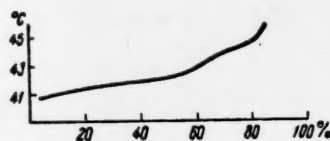


Fig. 1. Fractionation curve of catalyzate from cyclopentene.

TABLE 2

Boiling point in °C (753 mm)	Yield of fraction		Properties of fraction		Data from optical analysis *
	g	%	$n_D^{20}$	$d_4^{20}$	
41—42	63.7	53.0	1.4420	0.7968	Cyclopentadiene with a little cyclopentene Mixture of cyclopentadiene and cyclopentene in equal amounts Cyclopentene (about 75%) and cyclo- pentadiene (about 25%)
42—43	20.5	17.1	1.4360	0.7867	
43—45	13.2	11.0	1.4260	0.7793	
Residue	19.4	16.0	1.5100	—	
Losses	—	2.9	—	—	

The carbonaceous deposits on the catalyst were analyzed and found to approximate to a polymer of cyclopentadiene ( $C_5H_6$ )<sub>x</sub> (found %: C 90.81; H 9.19; calculated for  $C_5H_6$  %: C 90.84; H 9.16).

The gaseous products contained hydrogen (25%), ethane (16%), ethylene (23%), propane (20%), propylene (13%) and butadiene (3%).

It is interesting to note that the liquid reaction products did not contain cyclopentane, although this had been found by Plate [1,2] on dehydrogenation of cyclopentene at atmospheric pressure. Apparently, translocation of hydrogen hardly takes place at reduced pressure. The presence of ethane and propane among the gaseous products indicates, however, that these hydrocarbons could have been formed by hydrogenation of fragments of the cyclopentene molecule.

\* The optical analysis was carried out by Yu. P. Egorov to whom we convey our thanks.



The experiments have consequently shown that by conducting the dehydrogenation of cyclopentene under reduced pressure over a dehydrogenation catalyst we can substantially suppress side reactions and obtain a high yield of cyclopentadiene (up to 53% on the cyclopentene taken). Apart from dehydrogenation, the performance of the reaction under the specified conditions leads only to slight formation of coke and hydrocracking of cyclopentene with formation of gaseous products consisting predominantly of  $C_2$  and  $C_3$  compounds.

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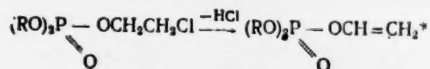
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# SYNTHESIS AND INVESTIGATION OF SOME VINYL ESTERS OF PHOSPHORUS ACIDS

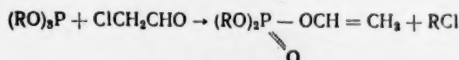
E. L. Gefter and Associate Member Acad. Sci. USSR

M. I. Kabachnik

Vinyl esters of phosphorus acids, which have recently become well known compounds, were first synthesized by the dehydrochlorination of the corresponding  $\beta$ -chloroethyl esters [1].

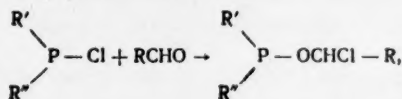


and somewhat later by the reaction of esters of trivalent phosphorus acids with chloroacetaldehyde [3] (according to Perkow [4]).



In the present article, a new method is described for the synthesis of vinyl esters of phosphorus acids, the method being based on the reaction of the chlorides of these acids with acetaldehyde and triethylamine. In developing this method, we proceeded from the following considerations:

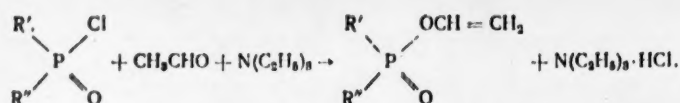
Kabachnik and Shepeleva [5-7], investigating the reaction of the chlorides of trivalent phosphorus acids with aldehydes, came to the conclusion that in this process the first stage, which proceeds at a low temperature, is the formation of  $\alpha$ -chloroalkyl esters of the corresponding acids,



which, with an increase in temperature, undergo further changes. The formation of products of the addition of an aldehyde to a phosphorus halide was confirmed by Faizullin and Trifonov [8] (for the case of benzaldehyde and phosphorus trichloride) by physicochemical analytical methods.

We assumed that the addition to the aldehyde-phosphorus halide system of a strong organic base would direct the reaction toward the formation of vinyl esters of phosphorus acids according to the scheme:

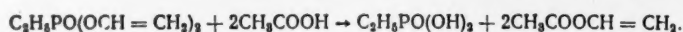
\* Allen and coworkers [2] considered these results to be in error after unsuccessful attempts to reproduce them.



This proposal was confirmed by experiment [9].

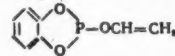
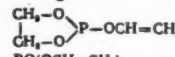
The reaction was carried out by the action of an excess of acetaldehyde and triethylamine on chlorides of phosphorus acids with external cooling and good agitation. A white, crystalline precipitate, which turned red with time, was formed. The volatile fraction was distilled (at 20-100 mm) from the reaction flask, and then, on further heating at 2-10 mm the vinyl ester of the corresponding phosphorus acid came over. At times, the precipitate was filtered before the distillation; however, this had no effect on the yields. For the removal of traces of triethylamine, the distilled product was mixed with several drops of phosphoric acid and, after some time, was distilled again.

In addition to the analytical data, saponification of certain of the esters to the corresponding phosphorus acids and transesterification with acetic acid to give vinyl acetate proved the structure of the vinyl esters of phosphorus acids.



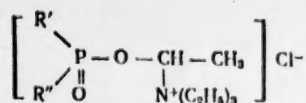
By means of the method described in the present communication, we synthesized a series of new vinyl esters of substituted phosphorous and phosphinic acids as well as trivinyl phosphate (Table 1).

TABLE 1

Formula	B.p., °C/mm	$d_4^{20}$	$n_D^{20}$	$MR_D$	
				Found	Calc.
$\text{CH}_3\text{P}(\text{OCH}=\text{CH}_2)_3$	64-65/8	1.1097	1.4394	35.14	35.22
$\text{C}_2\text{H}_5\text{PO}(\text{OCH}=\text{CH}_2)_2$	60-61/5-5.5	1.0707	1.4409	39.99	39.84
$\text{ClCH}_2\text{P}(\text{OCH}=\text{CH}_2)_2$	66-67/1	1.2458	1.4636	40.41	40.09
$\text{CH}_2=\text{CHPO}(\text{OCH}=\text{CH}_2)_2$	49-50/1.5-2	1.1020	1.4530	39.28	39.37
$\begin{array}{c} \text{OCH}_2\text{CH}_2\text{Cl} \\   \\ \text{CH}_2\text{P}=\text{O} \\   \\ \text{OCH}=\text{CH}_2 \end{array}$	96-98/3.5-4	1.2351	1.4540	40.48	40.56
$\begin{array}{c} \text{OC}_2\text{H}_5 \\   \\ \text{CH}_2\text{P}=\text{O} \\   \\ \text{OCH}=\text{CH}_2 \end{array}$	63-65/2.5-3	1.0208	1.4278	44.89	44.92
$\text{C}_2\text{H}_5\text{P}(\text{OCH}=\text{CH}_2)_2$	110-111/1.5-2	1.1589	1.5144	54.64	54.54
$\text{C}_6\text{H}_5\text{P}(\text{O})\text{OCH}=\text{CH}_2$	102-104/2	1.1166	1.5224	50.04	49.33
	71/2-2.5	1.2306	1.5357	46.19	45.94
	58-59/15	1.1672	1.4577	31.34	31.07
$\text{PO}(\text{OCH}=\text{CH}_2)_3$	84-85/10	1.1240	1.4314	40.60	40.50

Note. Analyses of the substances synthesized agreed well with the calculated values.

The yields from this reaction were relatively low. Regardless of variations in the synthesis conditions, it did not exceed 30-35% of theoretical. A large residue, which decomposed on further heating, always remained in the distillation flask. It is absolutely necessary to use carefully purified starting materials and also an excess of the aldehyde and amine; otherwise, the yields fall off sharply, sometimes to zero. As regards the mechanism of the formation of the vinyl esters of phosphorus acids, it can be hypothesized that an  $\alpha$ -chlorinated ester is first formed, and this gives an unstable complex with the



triethylamine (in case trimethylamine is used in place of the triethylamine, the complex is of such a nature that it can be isolated and analyzed). Decomposition of the complex leads to the formation of the vinyl ester of the phosphorus acid and triethylamine hydrochloride (and other unidentified products which are contained in the distillation residue). Sladkov and Petrov [10], carrying out an analogous reaction in the carboxylic series, assumed that the aldehyde first isomerized to the corresponding vinyl alcohol which then reacted with the acid chloride. Such an assumption seems scarcely probable to us in view of the extremely slight tendency of acetaldehyde toward enolization.

The ability to polymerize characterized these vinyl esters of phosphorus acids, as was shown by some preliminary experiments, described below. The polymerization was carried out in carefully washed glass ampoules using benzoyl peroxide, recrystallized from chloroform, as the initiator. After placing the initiator and material in the ampoule, the latter was held for 10-15 minutes at 15-20 mm pressure, after which it was sealed in a vacuum and placed in a thermostatted bath the temperature of which was either gradually increased from 50 to 70-80° or maintained constant. The polymerization conditions and nature of the polymers are presented in Table 2.

TABLE 2

Formula	Benzoyl peroxide, %	Polymerization temperature, °C	Time, hours	Nature of polymer
$\begin{array}{c} \text{OC}_2\text{H}_5 \\   \\ \text{CH}_3\text{P} \\   \\ \text{O} \\   \\ \text{OCH}=\text{CH}_2 \end{array}$	1.45-1.84	50-70	200	Light yellow liquid
$\begin{array}{c} \text{OCH}_2\text{CH}_2\text{Cl} \\   \\ \text{CH}_3\text{P} \\   \\ \text{O} \\   \\ \text{OCH}=\text{CH}_2 \end{array}$	1.5	50-70	150	Yellow, soft. Swells and slowly dissolves in chloroform
$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{CH}_2 \\   \\ \text{P}(\text{O})\text{OCH}=\text{CH}_2 \end{array}$	1.5	50-80	200	Dark yellow, thick liquid
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{P}-\text{OCH}=\text{CH}_2 \end{array}$	0.9	50-70	120	Yellow, soft. Swells in chloroform
$\begin{array}{c} \text{CH}_3-\text{O} \\   \\ \text{CH}_2-\text{O} \\   \\ \text{P}-\text{OCH}=\text{CH}_2 \end{array}$	1.24	50-70	200	Dark, soft. Swells and slowly dissolves in chloroform
$\text{CH}_3\text{PO}(\text{OCH}=\text{CH}_2)_2$	1.4-1.9	50	50	Light yellow, solid, incombustible, insoluble
$\text{C}_2\text{H}_5\text{PO}(\text{OCH}=\text{CH}_2)_2$	1.3	50-70	100	Light yellow, solid, incombustible, insoluble
$\text{ClCH}_2\text{PO}(\text{OCH}=\text{CH}_2)_2$	0.67	50	30	Yellow, solid, incombustible, insoluble
$\text{C}_6\text{H}_5\text{PO}(\text{OCH}=\text{CH}_2)_2$	1.2	50	150	Black, solid, incombustible, insoluble
$\text{CH}_2=\text{CHPO}(\text{OCH}=\text{CH}_2)_2$	0.7	70	30	Yellow, solid, incombustible, insoluble
$\text{PO}(\text{OCH}=\text{CH}_2)_3$	1	50-70	5	Yellow, solid, incombustible, insoluble
	1	50-70	100	

From the data presented in Table 2, it can be concluded that the esters containing one double bond form comparatively low molecular weight, linear polymers.

Esters containing two and three double bonds polymerize considerably more rapidly and form cross-linked polymers insoluble in organic solvents.

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\* Original Russian pagination. See C.B. Translation.



# REDUCTION OF MONOOLEFINIC HYDROCARBONS WITH ALKALI METALS IN A LIQUID AMMONIA MEDIUM

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and Academician B.A. Kazansky

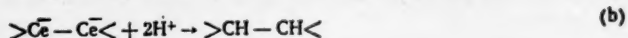
Until recently, it has been considered that hydrogen "at the instant of liberation" can reduce only those double bonds,  $>C=C<$ , which are conjugated either with other double bonds or with an aromatic nucleus.

In recent years, a number of facts have become established concerning the reduction of isolated olefinic double bonds by so-called hydrogen at the instant of liberation. Thus, Hackspill and Rohmer [1] observed that metallic cesium can add to ethylene, and the resulting compound is converted to ethane by the action of steam. Kazansky and Gostunskaya [2,3] partially reduced 2-methyl-1-butene, 2-methyl-2-butene, 2,5-dimethyl-2-hexene, 2,5-dimethyl-3-hexene, and cyclohexene, by means of hydrogen liberated during the decomposition of calcium hexammine according to the equation  $Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + 2H$ . Orchin and coworkers [4] partially reduced 1-hexene by the action of sodium dissolved in liquid ammonia in the presence of methyl alcohol. Benkeser and coworkers [5,6] obtained saturated hydrocarbons by the action on cyclohexene and 5-decene of lithium in media of the simplest aliphatic amines.

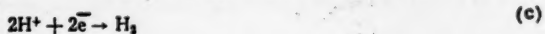
Still, Kraus [7,8] and, later, Barton and Ingold [9] and Birch [10] proposed that the addition of hydrogen to a double bond by the action of sodium dissolved in liquid ammonia be considered an ionic reaction. According to Kraus and to Birch, the first stage of the reaction is the addition to the double bond of one or two electrons, the source of which is the metal dissolved in ammonia:



In the second stage, protons are added to the resulting carbanion, ammonia, amines, alcohols, and other protolytic agents serving as the source of the protons:



A side reaction resulting in the liberation of hydrogen can proceed simultaneously with the reduction:



The effect of the nature and structure of the olefin and of the nature of the metal and the alcohol on the rate of reduction of monoolefins of the aliphatic series in a liquid ammonia medium was investigated in the present work. Monoolefins of normal structure were used in the investigation: 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 2-octene, and 3-heptene. Na, Li, and K were used as the metal reducing agents; methyl and ethyl alcohols were added as proton donors. Na in liquid ammonia in the presence of methyl alcohol comparatively readily reduced 1-pentene, 1-hexene, and 1-heptene (with an average yield of about 40%); 1-octene was reduced more slowly (with a yield of 20%); 1-nonene and 1-decene were reduced considerably more difficultly (3-6% yields). Reaction (c) proceeding more markedly with them;

olefins with an internal double bond (3-heptene and 2-octene) were not reduced at all. An increase in the concentration of methyl alcohol led to an increase in the liberation of free hydrogen (Reaction (c)) and to a decrease in the yield of saturated hydrocarbon. On replacing the methyl alcohol with the less acidic ethyl alcohol (dissociation constant 100 times less than that of methyl [11, 12]), the reduction reaction proceeded more rapidly. Under these conditions, 1-nonene and 1-decene were reduced 20% and 8%, respectively.

When K or Li in liquid ammonia was used as the reducing agent in the presence of methyl alcohol, the enumerated monoolefins were reduced more slowly than in the presence of Na under the same conditions. However, their comparative reactivity in the reduction reaction does not correspond to their positions in the electromotive series in liquid ammonia. This series is [13]:  $\text{Na} < \text{K} < \text{Li}$ .

The more intense liberation of free hydrogen by potassium and lithium must lower the rate of reduction of the olefins investigated, since the rate of their reduction is less than the rate of the concurrent reaction liberating free hydrogen.

### EXPERIMENTAL

The 1-pentene (b.p. 30.0°/760 mm,  $n_D^{20}$  1.3718,  $d_4^{20}$  0.6411) and 1-heptene (b.p. 93.7°/760 mm,  $n_D^{20}$  1.3995,  $d_4^{20}$  0.6965) were prepared from allyl chloride and the appropriate alkylmagnesium halide. The 1-hexene (b.p. 63.2°/760 mm,  $n_D^{20}$  1.3876,  $d_4^{20}$  0.6735), 3-heptene (b.p. 95.7-95.8°/760 mm,  $n_D^{20}$  1.4048,  $d_4^{20}$  0.7002), 1-octene (b.p. 121.3°/760 mm,  $n_D^{20}$  1.4092,  $d_4^{20}$  0.7155), 2-octene (b.p. 124.7-125.2°/760 mm,  $n_D^{20}$  1.4140,  $d_4^{20}$  0.7215), 1-nonene (b.p. 146.6°/760 mm,  $n_D^{20}$  1.4158,  $d_4^{20}$  0.7292) and 1-decene (b.p. 170.7°/760 mm,  $n_D^{20}$  1.4215,  $d_4^{20}$  0.7410) were prepared by pyrolysis of the acetates of the corresponding alcohols. Their constants agree with the most reliable literature data [14].

#### Method of Reduction of the Olefins and Investigation of the Reaction Products.

The reaction was carried out in an 0.5-liter three-necked flask fitted with an effective stirrer, a thermometer, a tube, extending to the bottom of the flask, for the introduction of gaseous ammonia, and a short tube connected with a drying tube filled with pieces of solid potassium hydroxide. The flask was cooled with a mixture of dry ice and ethyl alcohol in a Dewar flask.

Reduction of the olefins was carried out by two methods.

**Method A.** To the flask containing 150 ml of liquid ammonia was added, with vigorous stirring, small pieces of the metal (0.2 g-atom) until a homogeneous solution was formed. Then at -35, -37° a solution of the hydrocarbon in alcohol (0.1 mole of hydrocarbon and 0.25 mole of alcohol) was added dropwise over a 40-minute period. Stirring was continued for another hour at the same temperature; by this time, practically all of the metal had reacted; liberation of free hydrogen ceased 50-60 minutes after initiation of the reaction. Then 12-20 ml of ether (in the case of 1-pentene, 1-hexene, and 1-heptene, the ether was replaced by dibutyl ether) was added to the flask, and, with intense cooling and stirring, slow decomposition of the reaction mixture with ice and then partial neutralization of the ammonia with carbon dioxide was carried out. The ether layer was washed with water, dilute hydrochloric acid, and again with water, and dried over  $\text{CaCl}_2$ . After distillation of the ether, the hydrocarbon was distilled over sodium from a Favorsky flask or in a column of 40 theoretical plates and investigated. The per cent reduction was calculated from the change in index of refraction and the bromine number, which was determined by the method of Kaufman-Galpern-Vinogradova [15].

**Method B.** The hydrocarbon and alcohol (in the same amounts as in the experiments by Method A) were placed in the flask with the liquid ammonia, and the metal (0.2 g-atom) was introduced in pieces through a neck of the flask with vigorous stirring over a period of 40 minutes. Further operations were as in Method A.

In none of the experiments did the results of the reduction depend on the order of addition of the reagents.

#### Results of the Reduction of the Monoolefins.

1-Pentene, 1-hexene, and 1-heptene were reduced both by Method A and by Method B; 1-octene, 1-nonene, and 1-decene were reduced only by Method B. The indices of refraction and the bromine numbers of the products of reduction in the presence of methyl alcohol are presented in Table 1.

TABLE 1

Hydrocarbon	Na + NH <sub>3</sub> + CH <sub>3</sub> OH			K + NH <sub>3</sub> + CH <sub>3</sub> OH			Li + NH <sub>3</sub> + CH <sub>3</sub> OH		
	$n_D^{20}$	Bromine number	% re-duction	$n_D^{20}$	Bromine number	% re-duction	$n_D^{20}$	Bromine number	% re-duction
1-Pentene	1.3655	144.2	43	1.3707	166.8	13	1.3670	157.0	32
1-Hexene	1.3893	113.8	40	1.382	168.1	11	1.3850	149.3	23
1-Heptene	1.3946	101.2	38	1.3984	140.5	9	1.3975	140.2	15
1-Octene	1.4067	113.8	20	1.4181	131.9	7	1.4079	130.4	9
1-Nonene	1.4150	110.5	6	1.4151	120.4	5	1.4154	124.6	2
1-Decene	1.4210	110.5	3	1.4212	112.0	2	1.4216	116.0	0

All of the hydrocarbons were also reduced by sodium in liquid ammonia and in the presence of ethyl alcohol (Table 2).

TABLE 2

Hydrocarbon	Na + NH <sub>3</sub> + CH <sub>3</sub> CH <sub>2</sub> OH		
	$n_D^{20}$	Bromine number	% Paraffin
1-Pentene	1.3651	128.3	45
1-Hexene	1.3820	111.2	42
1-Heptene	1.3942	95.9	41
1-Octene	1.4158	101.0	30
1-Nonene	1.4155	112.0	20
1-Decene	1.4206	106.0	8

As seen from these data, reduction is deeper in the presence of ethyl alcohol.

3-Heptene and 2-octene were subjected to reduction by Na and K in liquid ammonia with the addition of methyl and of ethyl alcohol. In all experiments, the bromine numbers of the reaction products were almost unchanged in comparison with those of the original hydrocarbons, which indicates that reduction did not occur. Some lowering of the values of  $n_D^{20}$  and  $d_4^{20}$  could also be explained by partial conversion of cis-olefins to trans-olefins [16], since the original hydrocarbons were, in all probability, mixtures of these stereoisomeric forms. The experimental data and the constants of the respective trans-isomers are presented in Table 3.

In order to clarify whether there was any shifting of the double bonds of the  $\alpha$ -olefins to the center of the molecule, which would decrease the yield of reduction products, we reduced 1-heptene and 1-octene with Na in liquid ammonia with the addition of methyl alcohol.

TABLE 3

Hydrocarbon	Before the experiment			After the experiment			Lit. data for trans-isomers [15]	
	$n_D^{20}$	$d_4^{20}$	Bromine number	$n_D^{20}$	$d_4^{20}$	Bromine number	$n_D^{20}$	$d_4^{20}$
3-Heptene	1.4048	0.7002	162.9	1.4046	0.6992	161.4	1.4043	0.6981
2-Octene	1.4140	0.7215	142.5	1.4133	0.7210	141.5	1.4132	0.7199

During distillation of the reduction products in an 80-plate column, no unsaturated fractions were isolated with a boiling point corresponding to 2-pentene (98°), 3-heptene (95.7°), 2-octene (125°) or 3-octene (123°). The fractions obtained corresponded to the original olefins and the products of their reduction - n-heptene and n-octane.

The distillation results are presented in Table 4.

TABLE 4

Hydrocarbon	Fraction I			Fraction III			
	B. p. °C	$n_D^{20}$	Bromine number	B. p. °C	$n_D^{20}$	$d_4^{20}$	Bromine number
1-Heptene	93.7-93.7	1.3993	161.8	98.5	1.3873	0.6882	2
1-Octene	121.3-121.4	1.4086	141.6	125.6	1.3976	0.7021	0.8

## CONCLUSIONS

1. In the reduction of  $\alpha$ -olefins by alkali metals in liquid ammonia in the presence of alcohol, the yield of saturated hydrocarbons decreases with an increase in the molecular weight of the olefin.
2. Under the conditions investigated, olefins with the double bond in the  $\beta$ - or  $\gamma$ -position are not reduced.
3. Of the three alkali metals used, Li, Na, and K, the most active in the reduction reaction was Na.
4. Replacement of methyl alcohol by the less acidic ethyl alcohol during the reduction of  $C_6$ - $C_{10}$  olefins increased the yield of saturated hydrocarbons.

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# PREPARATION OF HIGHER $\alpha, \alpha, \alpha, \omega$ -TETRACHLOROALKANES IN A FLOW APPARATUS

Sh. A. Karapetyan and L. A. Pichugin

(Presented by Academician A. N. Nesmeyanov, February 19, 1957)

The possibility of synthesizing higher tetrachloroalkanes at pressures of 100-150 atm. has previously been shown, and the quantitative dependence of product distribution on pressure and relative concentration of ethylene was evaluated [1]. An apparatus for the continuous production of tetrachloroalkanes and more precise conditions for carrying out the process are described in the present article.

TABLE 1

Exp. No.	Temperature, °C	Time, min.	CCl <sub>4</sub> conversion, %	Composition of tetrachloroalkane mixture			
				C <sub>5</sub>	C <sub>7</sub>	C <sub>9</sub>	C <sub>&gt;9</sub>
1	90	15	15	34.5	27	23	15.5
2		30	24.5	38.3	30.8	18.5	12.5
3		60	36	32	31	17	18.5
4		120	47	33	31	16	18.5
Average				34.5	30	19	16.3
5	100	15	24	41	31.7	13.7	11.3
6		30	30	43	29.7	14	11
7		60	31.3	41.5	31	15	10.5
8		120	33.5	42.5	28	15.5	11.5
Average				41.8	30.4	13.4	11
9	80	60	28	16	21	17	46
10	50	120	45	17	24	18	41
11	90	30	31	—	—	—	—
12	90	60	54	20.8	26	19	34.5
13	90	120	66.5	21	26.2	16.5	36.5
14	100	15	30	—	—	—	—
15	100	30	41	—	—	—	—
16	100	60	44	33	23	14	30
17	100	120	44	—	—	—	—

Note: 1. Experiments 1-8: 0.35-liter autoclave, 120 atm.

press, ethylene/CCl<sub>4</sub> =  $\frac{3.2}{0.8}$  = 4 moles/mole; Experiments 9-17: 0.5- and 2.7-liter autoclaves, 150 atm. press., ethylene/CCl<sub>4</sub> = 10 moles/mole.

2. In Experiments 5-8 at 100°, 2.5-3% tetrachloropropane (C<sub>3</sub>).

The effect of temperature and reaction time was studied in rocking autoclaves fitted with electrical heaters and water jackets, which permitted regulation of the temperature to 1°. Constant pressure was maintained by feeding ethylene to the autoclave at its consumption rate. The deviation in ethylene charged



as measured by two independent methods was  $\pm 3.3\%$  in each separate experiment and  $0.2\%$  for the series of 17 experiments. Azobisisobutyronitrile in a concentration of 1 g per liter of autoclave volume was used as the reaction initiator. The mixture of tetrachloroalkanes was separated by vacuum rectification.

In Table 1 and in Figure 1 are shown averaged results from a large number of experiments; it is seen that at  $100^\circ$  the reaction is practically complete after 20-30 minutes, but the conversion of  $\text{CCl}_4$  is significantly less than at  $90^\circ$ . It was established that the composition of the mixture of tetrachloroalkanes depends on temperature, an increase in temperature increasing the content of lower ( $\text{C}_3$ ) and decreasing the amount of higher ( $\text{C}_8$  and  $>\text{C}_8$ ) telomers.

The experiments described here and earlier [1] were carried out in autoclaves of different diameters (35, 50, and 100 mm). No appreciable effect of reactor dimensions on conversion and composition was observed. In a special series of experiments in a flow reactor of 4-mm diameter and in an 0.5-liter autoclave packed with  $10 \times 10$  mm, glass rings, no substantial, regular difference was detected in comparison with experiments in the same autoclave under equivalent conditions but without packing (Table 2).

TABLE 2

Temp. °C	Press., Atm.	Duration hours	Ethylene/ CCl <sub>4</sub> , mole/mole	CCl <sub>4</sub> con- version, %	Composition of tetrachloroalkane mixture, %				
					C <sub>3</sub>	C <sub>5</sub>	C <sub>7</sub>	C <sub>9</sub>	
0.5-Liter autoclave, 50-mm diameter									
90	120	1	2.2	43	5	47	28	12	8
		1	3.3	33	2	40	32	16	10
		1	4.5	42	—	38.5	30	16.5	15
100	150	1	9.7	51	—	21	24	21	34
	120	0.5	4.1	30	3	42	30	14	11
		1	3.9	31	2.5	41.5	31	15	10
0.5-Liter autoclave with 10 × 10-mm packing									
90	120	1	2.2	41.5	5	45.5	30	12	7.5
		1	3.7	36.5	2.5	41	29	14.5	13
		1	4.7	43	—	40.5	30	15.5	14
	150	1	10	55	—	21	24	18	37
Coil, 70-ml volume, 4-mm diameter*									
100	120	0.5—1	2.6	28.8	—	—	—	—	—

\* Reaction carried out in flow apparatus. In 3 hours, 180 g  $\text{CCl}_4$  and 84.5 g ethylene were charged and 80 g tetrachloroalkanes was obtained.

When the entire quantity of initiator is charged at once, it is not completely used and the temperature jumps, lowering conversion. Gradual feeding of the initiator during the process should create a uniform concentration of initial radicals, bring about more complete usage of the initiator, and increase conversion. This proposition was confirmed in experiments in which the initiator was fed uniformly (0.53 g per 38 ml  $\text{CCl}_4$ ) through a 1-mm diameter capillary tube into a rocking autoclave containing ethylene and  $\text{CCl}_4$  (3 moles/mole) at 120 atm. It is seen from Table 3 that with protracted, uniform feeding of the initiator, conversion increased by a factor of 1.5 in comparison with short-term feeding.

TABLE 3

Initiator feeding time, min.	Tempera- ture °C	Conver- sion $\text{CCl}_4$ , %	Sp. gr. of telomer mixture
8	100	24	1.254
30		37	1.263
5	100-115	19	1.261
30		29	1.263

The telomerization flow systems described in the literature [2-4] differ essentially in the method of recycling the unreacted ethylene to the reactor and in the construction of the latter. Taking into account the critical constants of ethylene and the data of Efremova and Leontyeva [5], a system for the circulation of ethylene under a pressure of 40-60 atm. and with a separator temperature of  $90-120^\circ$  was proposed and calculated [6]. The circulation system is improved if the  $\text{CCl}_4$  is fed to the mixing tank, not to the reactor [4]. In this way, the critical temperature of the mixture is increased and the operation of the circulating pump is improved.



The data obtained in this work were used in the construction of a continuous flow apparatus for the synthesis of higher tetrachloroalkanes; a schematic diagram of the apparatus is shown in Figure 2. The stainless steel reactor, constructed of 58/50-mm standard tubing, had six sections with intermediate taps and thermowells in each section. Such construction permitted a study of the dynamics of the process, and initiator was uniformly fed to all sections in order to obtain an increase in conversion and a smooth reaction.

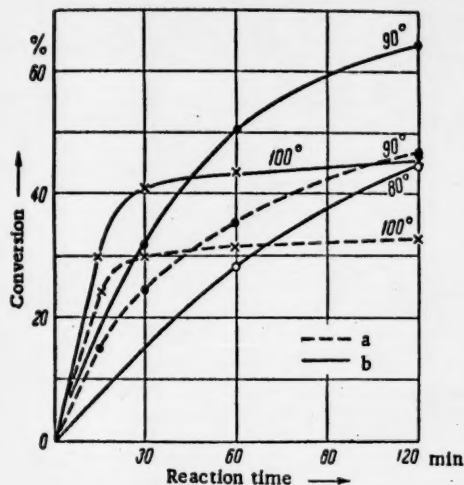


Fig. 1. Effect of time and temperature on  $\text{CCl}_4$  conversion at mole ratios of ethylene to  $\text{CCl}_4$  of 4 (a) and 10 (b).

In this apparatus, a series of continuous experiments was carried out on the synthesis of higher tetrachloroalkanes (TCA), the experiments being directed toward obtaining the maximum amount of  $\text{C}_9 - \text{C}_{15}$  fraction.

Experimental conditions: pressure, 140-150 atm.; temperature, 90-95°; initiator concentration, 8-10 g/liter  $\text{CCl}_4$ , corresponding approximately to 0.5-0.8 g/liter of reactor volume; relative concentration of ethylene, 10-11.5 moles/mole of  $\text{CCl}_4$ . In Table 4 are presented the results of 7 experiments of 4-8 hours duration, each under the above conditions.

The ethylene content of the reaction products was, according to the analytical data, 41% or 24.5 kg, which gives a consumption of 3.5%, based on the amount charged, with an overall loss of material of 1.8%. The composition of the mixture of telomers agreed very satisfactorily with the data from the autoclave experiments (see Table 1). From a combined sample of residues left after rectification in a column there was separated a fraction of higher tetrachloroalkanes,  $\text{C}_{11} - \text{C}_{15}$ , in amounts of 23% in the autoclave experiments

and 18-22% in the flow experiments (calculated on the original telomer mixture), which is somewhat lower than the maximum possible amount [1].

TABLE 4

No. Exp.	Feed, kg			Reactor effluent				Composition of TCA mixture, %			
	$\text{CCl}_4$	$\text{C}_2\text{H}_4$	Total	Amount kg	Sp. gr.	TCA content		$\text{C}_5$	$\text{C}_7$	$\text{C}_9$	$\text{C}_{>9}$
						kg	%				
1	9.7	2.3	12.0	11.0	1.35	5.3	48	22	26	22	30
2	20.4	5.9	26.3	26.5	1.39	12.2	46	25	22	15	38
3	11.4	1.9	13.3	13.2	1.35	7.2	55	22	25	17	36
4	11.8	3.5	15.3	15.7	1.38	7.7	49	23	20	22	45
5	12.9	3.1	16.0	16.3	1.38	7.6	46				
6	13.2	3.7	16.9	16.1	1.35	8.3	51				
7	18.3	5.0	23.3	22.1	1.36	11.6	52				
Total	97.7	25.4	123.1	120.9	1.365	59.9	49.6				

The absence of appreciable losses, the good agreement of the ethylene balance, the small deviations of the results of individual experiments from average values show that the process of synthesizing higher tetrachloroalkanes was stably reproduced in the apparatus at pressures below 150 atm. and with increased concentrations of ethylene and initiator.

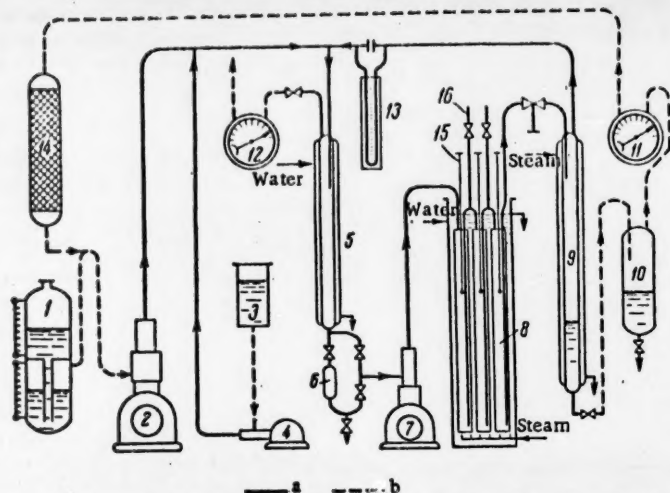


Fig. 2. Schematic diagram of the flow apparatus: 1) calibrated gas holder, 2) compressor, 3) calibrated  $\text{CCl}_4$  tank, 4) proportioning pump, 5) condenser-mixer, 6) sampler, 7) circulating pump, 8) reactor, 9) separator, 10) TCA accumulator, 11) 12) gas meters, 13) high-pressure flow meter, 14) adsorber, 15) thermocouple, 16) intermediate taps: a) high pressure (50-150 atm.), b) low pressure (0.1-0.3 atm.).

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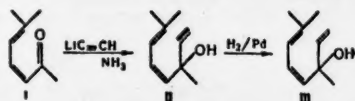
# ANIONOTROPIC REARRANGEMENT OF 2,6-DIMETHYL-2,4,7-OCTATRIEN-6-OL

Academician I. N. Nazarov, Zh. A. Krasnaya and S. M. Makin

An interesting characteristic of polyenic alcohols is that under the influence of dilute acids they very readily undergo anionotropic rearrangement with a shift of the hydroxyl and an increase in the number of conjugated bonds [1]. An investigation of this rearrangement is of interest from the point of view of the possibility of preparing primary alcohols, especially of the isoprenoid type.

We investigated the anionotropic rearrangement of 2,6-dimethyl-2,4,7-octatrien-6-ol (III), which in carbon chain structure is an analog of linalool with one additional double bond.

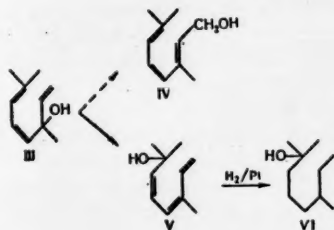
The previously undescribed 2,6-dimethyl-2,4-octadien-7-yne-6-ol (II) was obtained in good yield by the action of lithium acetylide in liquid ammonia on 2-methyl-2,4-heptadien-6-one (I).



By the absorption of 1 mole of hydrogen in the presence of Pd catalyst, carbinol II was converted to 2,6-dimethyl-2,4,7-octatrien-6-ol (III), a liquid with an agreeable flower fragrance.

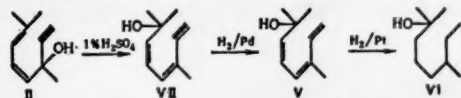
The anionotropic rearrangement of carbinol III can take two directions; either the formation of a primary alcohol (dehydrogeraniol) by shifting one double bond, or

the formation of the tertiary alcohol V by simultaneous shifting of two double bonds.



We established that the action on carbinol III of 0.05% sulfuric acid for 1.5 hours at room temperature gives only the tertiary alcohol V; primary alcohol IV is not formed.

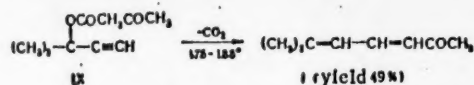
For proof that the reaction follows this course, the V obtained was subjected to exhaustive hydrogenation to 2,6-dimethyl-2-octanol (VI), and then this same alcohol VI was obtained by the following reactions:



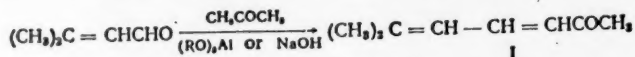
2,6-Dimethyl-2,4-octadien-7-yne-6-ol, which can undergo anionotropic rearrangement only with the formation of a tertiary alcohol, isomerizes to 2,6-dimethyl-3,5-octadien-7-yne-2-ol (VII) under the action of 1% sulfuric acid. On partial hydrogenation in the presence of Pd catalyst, the latter carbinol is converted to V, and on complete hydrogenation in the presence of Pt catalyst it is converted to VI. The saturated alcohol VI obtained by both methods gives 3,5-dinitrobenzoates (molecular compounds with  $\alpha$ -naphthylamine) which melt at the same temperature (100-101°), and a mixture of the two samples melt without depression of the melting point.

The methylheptadienone I required for the synthesis of carbinol II was obtained by two routes:

1. By pyrolysis of the acetoacetate of dimethylethynylcarbinol [2, 3]:



2. By the condensation of dimethylacrylaldehyde with acetone under the influence of aluminum isopropoxide or tertiary amoxide (yield 68-72%) or of sodium hydroxide (yield 47.5%).



## EXPERIMENTAL

### Synthesis of 2-Methyl-2,4-Heptadien-6-one (I) From Dimethylethynylcarbinol (VIII)

a) Acetoacetate of dimethylethynylcarbinol (IX). 112 g of diketene (b. p. 51-52°/50 mm;  $n_D^{20}$  1.4350) was added with stirring over a period of 1.5 hours to a mixture of 120 g of dimethylethynylcarbinol (VIII) and 10 drops of triethylamine heated to 85°. The reaction mixture was stirred for 15 minutes at 85-95°, and was then distilled under vacuum. There was obtained 191 g (92% calculated on the diketene) of the acetoacetate of dimethylethynylcarbinol (IX) with a. b. p. of 90-92°/10 mm [2].

b) Pyrolysis of the acetoacetate of dimethylethynylcarbinol (IX). A mixture of 90 g of IX and 100 g of dry vaseline oil was heated at 175-185° for 5 hours. Continuous evolution of carbon dioxide was observed.

Toward the end of the experiment, the temperature began to fall gradually owing to the accumulation of a low-boiling liquid, and the evolution of carbon dioxide slowed down considerably. 12 g of liquid was distilled at 30-38° under a vacuum of 15 mm;  $n_D^{20}$ . The residue was heated 30 minutes at 190-210° until the evolution of gas ceased, and the product was distilled under vacuum. There was obtained 29 g of (I) with a. b. p. of 77-79°/7 mm;  $n_D^{20}$  1.5327 [4],  $\lambda_{\text{max}}$  (in isooctane) 275 m $\mu$ . Yield 49%.

The 2,4-dinitrophenylhydrazone of dienone I melted at 209-210° (from a mixture of ethyl alcohol with ethyl acetate)  $\lambda_{\text{max}}$  (in isooctane) 372 m $\mu$ .

The semicarbazone of dienone I melted at 174-175° (from ethyl alcohol)  $\lambda_{\text{max}}$  (in methanol) 295 m $\mu$  (log  $\epsilon$  4.746).

### Condensation of Dimethylacrylaldehyde with Acetone

a) Over a period of several minutes while cooling with tap water, 78.7 g of dimethylacrylaldehyde (b.p. 133-135°;  $n_D^{20}$  1.4525), was added to a suspension of 8 g of finely powdered sodium hydroxide in 650 ml of dry acetone, the temperature rising to 40° owing to exothermic heat. The mixture was stirred 10 minutes and the alkaline solution allowed to settle; the acetone solution was neutralized with solid carbon dioxide, dried, and distilled. The resulting raw ketone I, b. p. 50-60°/1 mm, was steam distilled and then redistilled under vacuum. There was obtained 55 g of dienone I, b. p. 56-59°/1 mm,  $n_D^{20}$  1.5310. Yield 47.5%.

b) A mixture of 10.7 g of dimethylacrylaldehyde, 260 ml of acetone, 500 ml of benzene, and 87 g of a 35% benzene solution of aluminum tertiary amoxide was heated at the boiling point in a stream of nitrogen for 40 hours. The mixture was cooled to 0°, and 200 ml of 10% sulfuric acid was added with stirring. The product was extracted with ether, washed with a 5% solution of sodium bicarbonate, then with water, dried with magnesium sulfate, and distilled. There was obtained 11.4 g (72% yield) of methylheptadienone I with a. b. p. of 57-59°/1 mm,  $n_D^{20}$  1.5301. With aluminum isopropoxide, the yield of methylheptadienone was 68%.

### Condensation of Acetylene with 2-Methyl-2,4-Heptadien-6-one

2,6-Dimethyl-2,4-octadien-7-yne-6-ol (II). The reaction was carried out in a 3-liter three-necked flask fitted with a mechanical stirrer, a gas-inlet tube for acetylene and ammonia, a thermometer, a dropping

• The ultraviolet spectra were obtained in the optical laboratory of Moscow State University.

funnel, and a drying tube filled with alkali.

1200 ml of dry liquid ammonia was condensed in the flask, which was cooled with a mixture of solid carbon dioxide and acetone. A vigorous stream of purified acetylene was passed into the ammonia, and, after 25 minutes, 6.5 g of finely shaved lithium was introduced into the stirred liquid over a period of 15 minutes. After 40 minutes, the originally black reaction mixture became milky, which indicated completion of the conversion of the lithium to the acetylide. The current of acetylene was considerably reduced, and, at a temperature of  $-70^{\circ}$  and with stirring, 57.3 g (0.46 mole) of methylheptadienone I in 250 ml of absolute ether was added to the lithium acetylide over a period of 2.5 hours. The reaction mixture was then stirred for 3 hours at  $-70^{\circ}$ , and was allowed to stand overnight with cooling. On the following day, cooling was discontinued, and the ammonia was evaporated. 300 ml of ether, 300 ml of water, and 60 g of ammonium chloride were added at a temperature of  $-5^{\circ}$ . The ether layer was separated, washed with water, dried with magnesium sulfate, and distilled. 55.7 g of carbinol II, b. p.  $52-61^{\circ}$  at 0.1 mm, was obtained. After purification of carbinol II from admixed methylheptadienone with semicarbazide, 35 g of 2,6-dimethyl-2,4-octadien-7-yne-6-ol (II), b. p.  $60-62^{\circ}$  at 0.05 mm, was isolated;  $n_D^{20}$  1.5120;  $d_4^{20}$  0.9055; MR found 50.07, calculated 46.91  $\lambda_{\max}$  (in isooctane) 239  $m\mu$  ( $\log \epsilon$  4.416), 274  $m\mu$  ( $\log \epsilon$  3.740). Yield 51%.

Found \* %: C 80.10; 80.17; H 9.62; 9.58  $C_{10}H_{14}O$ . Calculated %: 79.95; H 9.39

2,6-Dimethyl-2,4,7-octatrien-6-ol (III). 7.5 g (0.05 mole) of 2,6-dimethyl-2,4-octadien-7-yne-6-ol (II) was hydrogenated in 30 ml of absolute ethyl alcohol in the presence of Pd catalyst. The calculated amount (0.05 mole) of hydrogen (1240 ml,  $18^{\circ}$ /749 mm) was absorbed in 1 hour, and the hydrogenation was terminated. After distillation, there was obtained 6.9 g of 2,6-dimethyl-2,4,7-octatrien-6-ol (III) in the form of a colorless liquid with an agreeable flower odor, b. p.  $47-48^{\circ}$ /0.04 mm;  $n_D^{20}$  1.5039;  $d_4^{20}$  0.8804; MR found 51.14; calculated 48.50.  $\lambda_{\max}$  (in methanol) 273  $m\mu$  ( $\log \epsilon$  4.079), 280  $m\mu$  ( $\log \epsilon$  3.340).

Found \* %: C 78.05; 77.95; H 10.57; 10.60.  $C_{10}H_{16}O$ . Calculated %: C 78.85; H 10.58.

2,6-Dimethyl-3,5,7-octatrien-2-ol (V). A mixture of 4.2 g of 2,6-dimethyl-2,4,7-octatrien-6-ol (III), 60 ml of 0.05% sulfuric acid, and 0.01 g of hydroquinone was agitated 90 minutes at room temperature. The product was extracted with ether, washed with a 5% solution of sodium bicarbonate and then with water, dried, and distilled. There was obtained 3.0 g (72% yield) of 2,6-dimethyl-3,5,7-octatrien-2-ol (V), b. p.  $53-55^{\circ}$ /0.02 mm;  $n_D^{20}$  1.5311;  $d_4^{20}$  0.8945; MR found 52.61, calculated 48.50.  $\lambda_{\max}$  (in isooctane) 268  $m\mu$  ( $\log \epsilon$  4.528), 279  $m\mu$  ( $\log \epsilon$  4.428).

Found %: C 77.56; 77.70; H 10.52; 10.62  $C_{10}H_{16}O$ . Calculated %: C 78.85; H 10.58

1.52 g (0.01 mole) of carbinol (V) was subjected to exhaustive hydrogenation in 8 ml of absolute ethyl alcohol in the presence of Pt catalyst. 0.0294 mole of hydrogen (660 ml,  $18^{\circ}$ , 753 mm) was absorbed. Distillation gave 1.3 g of 2,6-dimethyl-2-octanol (VI), b. p.  $82-83^{\circ}$ /mm;  $n_D^{20}$  1.4352;  $d_4^{20}$  0.8335; MR found 49.72, calc. 49.90.  $\lambda_{\max}$  (in isooctane) 265  $m\mu$ .

Found %: C 75.77; 75.63; H 13.74; 13.63.  $C_{10}H_{22}O$ . Calculated %: C 75.86; H 14.00

The molecular compounds of the 3,5-dinitrobenzoate of alcohol (VI) with  $\alpha$ -naphthylamine melted at  $100-101^{\circ}$  (from ethyl alcohol).

Found %: N 8.84; 8.62.  $C_{27}H_{33}O_6N_3$ . Calculated %: N 8.47

2,6-Dimethyl-3,5-octadien-7-yne-2-ol (VII). A mixture of 8 g of 2,6-dimethyl-2,4-octadien-7-yne-6-ol (II), 54 ml of ether, 535 ml of 1% sulfuric acid, and 0.01 g of hydroquinone was stirred in an atmosphere of nitrogen for 5 hours at room temperature. The product was extracted with ether, washed with a solution of sodium bicarbonate and then with water, dried, and distilled.

There was obtained 6.3 g (79% yield) of 2,6-dimethyl-3,5-octadien-7-yne-2-ol (VII), b. p.  $59-62^{\circ}$ /0.05 mm;  $n_D^{20}$  1.5300;  $d_4^{20}$  0.9097. MR found 50.97; calculated 46.91.  $\lambda_{\max}$  (in isooctane) 262  $m\mu$  ( $\log \epsilon$  4.506).

\* The analysis was carried out immediately after distillation of carbinol II.

\*\* The low per cent carbon in this and other alcohols with several double bonds (see below) is explained by the high sensitivity of these compounds to atmospheric oxygen.



Found%: C 79.14; 79.01; H 9.00; 9.17.  $C_{18}H_{16}O$ . Calculated %: C 79.95; H 9.39

Hydrogenation of 2,6-Dimethyl-3,5-Octadien-7-yne-2-ol (VII)

2,6-Dimethyl-3,5,7-octatrien-2-ol (V) and 2,6-dimethyl-2-octanol (VI). 5.1 g (0.034 mole) of 2,6-dimethyl-3,5-octadien-7-yne-2-ol (VII) was hydrogenated in 15 ml of absolute alcohol in the presence of Pd catalyst. The calculated amount (0.034 mole) of hydrogen (860 ml 18°/739 mm) was absorbed in 2 hours and the hydrogenation was terminated. After distillation, there was obtained 4.1 g of 2,6-dimethyl-3,5,7-octatrien-2-ol (V), b. p. 55-56° at 0.02 mm;  $n_D^{20}$  1.5320;  $d_4^{20}$  0.8976; MR found 51.98 calc 48.50.  $\lambda_{max}$  (in isooctane) 267 m $\mu$  (log  $\epsilon$  4.399), 289 m $\mu$  (log  $\epsilon$  4.103).

Found %: C 78.19; 78.24; H 10.57; 10.63.  $C_{18}H_{16}O$ . Calculated %: C 78.91; H 10.59

3.1 g (0.02 mole) of 2,6-dimethyl-3,5,7-octatrien-2-ol (V) was subjected to exhaustive hydrogenation in 12 ml of absolute ethyl alcohol in the presence of Pt catalyst. 1480 ml of hydrogen (18°/739 mm) was absorbed, which corresponds to 2.9 moles of hydrogen per mole of carbinol. Distillation gave 2.9 g of dimethyl-2-octanol (VI), b. p. 81-83°/10 mm;  $n_D^{20}$  1.4352;  $d_4^{20}$  0.8333. The molecular compound of the 3,5-dinitrobenzoate of alcohol VI with  $\alpha$ -naphthylamine melted at 100-101° (from ethyl alcohol), and a mixed sample with the 3,5-dinitrobenzoate of alcohol VI described above melted without depression of the melting point.

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# SYNTHESIS AND CHEMICAL TRANSFORMATIONS OF TRICHLOROMETHYL AND $\omega,\omega$ -DICHLOROALLYL COMPOUNDS OF MERCURY

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and F. K. Velichko

Since organomercury compounds containing trichloromethyl and dichloroallyl groups are of interest from the point of view of the study of the chemical behavior of these groups, we investigated the possibility of synthesizing such compounds and studied some of their transformations.

While organomercury compounds containing trifluoromethyl [1] or triiodomethyl [2] groups have been described, attempts to synthesize trichloromethyl compounds by decarboxylation of mercury trichloroacetate [3] or by the photochemical reaction of carbon tetrachloride with mercury [4] failed.

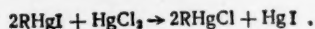
Not one representative of  $\omega,\omega$ -dihaloallyl organomercury compounds has been described in the literature up to the present time.

We studied the reaction of bromotrichloromethane, bromo- and iododichloromethane, and 1,1-dichloro-3-iodo-1-propene\* with mercury under u. v. irradiation at 70-80° and with vigorous stirring of the reaction mixture, and also the reaction of iodotrichloromethane with mercury simply with agitation of these reagents without irradiation. The following compounds were thereby obtained:  $\text{CCl}_3\text{HgBr}$ ,  $\text{CHCl}_2\text{HgBr}$ ,  $\text{CHCl}_2\text{HgI}$ ,  $\text{CCl}_2 = \text{CHCH}_2\text{HgI}$  and  $\text{CCl}_3\text{HgI}$  with yields of, respectively, 41; 1.2; 2.5; 67, and 12% of theoretical.

By the reaction of bromotrichloromethane with the calculated amount of 0.5% sodium amalgam, along with hexachloroethane, trichloromethylmercury was also obtained in small yield, while none of the symmetrical compound ( $\text{CCl}_3)_2\text{Hg}$  was formed. Such an anomaly is known only for cyclohexylmercury iodide [5].

In contrast to chloromethylmercury halides, which decompose with the liberation of mercury under the action of alkali [6], trichloromethylmercury bromide was converted by the action of moist silver oxide to the comparatively stable trichloromethylmercury hydroxide. Careful neutralization of an aqueous solution of  $\text{CCl}_3\text{HgOH}$  with hydrochloric or hydriodic acid gave  $\text{CCl}_3\text{HgCl}$  and  $\text{CCl}_3\text{HgI}$ . By this same route, the chloride and the bromide were prepared from  $\text{CCl}_2 = \text{CHCH}_2\text{HgI}$ .

We found a still simpler and more convenient method for the conversion of alkylmercury iodides to the chlorides, the method involving double decomposition with mercuric chloride while heating in ether or alcohol. The reaction proceeds according to:



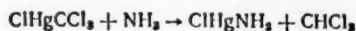
Among the reactions of trichloromethyl compounds of mercury, we may recall the so-called "quasi-complex" compounds. Trichloromethylmercury halides form complexes with pyridine, as do quasi-complex

\* Prepared from  $\text{CCl}_3 - \text{CH} = \text{CH}_2$  and also from  $\text{CCl}_2 = \text{CHCH}_2\text{Cl}$  by double decomposition with NaI in acetone, b.p. 69-70°/10 mm

Found %: C 15.29; 15.20; H 1.39; 1.57 Calculated %: C 15.21; H 1.28

compounds [7, 8]. In the case of  $\text{CCl}_3\text{HgI}$  the complex is unstable and decomposes rapidly on storage.

The action of dry ammonia on a chloroform solution of  $\text{CCl}_3\text{HgCl}$  did not form bistrichloromethylmercury, but an infusible precipitate was formed in 95.5% yield:



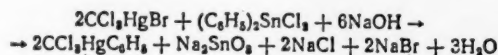
Ammonium chloride was not detected in the reaction mixture.

Hydrogen sulfide, even in the cold, quantitatively precipitated HgS from an alcoholic solution of trichloromethylmercury bromide.

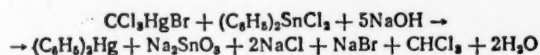
The reaction of trichloromethylmercury bromide with  $\text{C}_6\text{H}_5\text{MgBr}$  and  $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$  also proceeds in an unusual manner.

By the reaction of trichloromethylmercury bromide with  $\text{C}_6\text{H}_5\text{MgBr}$  under the usual conditions for the preparation of unsymmetrical organomercury compounds [9], along with phenyltrichloromethylmercury, phenylmercury bromide was obtained. A similar exchange of radicals between  $\text{RHgX}$  and  $\text{R'MgX}$  with the formation of  $\text{R'HgX}$  and  $\text{RMgX}$  has been noted in only a few cases [10-12].

The reaction of trichloromethylmercury bromide with diphenyltin dichloride under the usual conditions [13] proceeds in different directions depending on the amount of alkali used in the reaction. With a stoichiometric ratio of reagents, the reaction proceeded according to the equation:



forming phenyltrichloromethylmercury in 49% yield. With a larger amount of alkali, the reaction proceeded with the formation of diphenylmercury (29%), apparently according to the equation:



In both cases, a considerable formation of infusible and insoluble residues containing mercury was observed.

With a methanol solution of HCl, phenyltrichloromethylmercury formed  $\text{C}_6\text{H}_5\text{HgCl}$ , in quantitative yield, which indicates the high electronegativity of the trichloromethyl group relative to the phenyl group.  $\text{C}_6\text{H}_5\text{HgCl}$  (80%) was formed by half-hour heating of phenyltrichloromethylmercury at  $150^\circ$  in a sealed ampoule:



During an attempt to synthesize phenyltrichloromethylmercury by photochemical decarboxylation, at ordinary temperature, of  $\text{C}_6\text{H}_5\text{HgOCOCCL}_3$  (obtained from  $\text{C}_6\text{H}_5\text{HgOH}$  and  $\text{CCl}_3\text{COOH}$ ) in methanol, only phenylmercury chloride, along with unreacted reagent, was separated from the reaction mixture.

An analogous result was obtained on heating  $\text{C}_6\text{H}_5\text{HgOCOCCL}_3$  in a vacuum to  $240^\circ$  for several minutes.

The action of the usual "symmetrizers" ( $\text{KI}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Cu}$ ) on trichloromethylmercury halides did not lead to the formation of bistrichloromethylmercury.

Analytical data and the melting points of the organomercury compounds synthesized are presented in Table 1.

TABLE 1

Compound	M.p. °C	Found, %	Calculated, %
$\text{CCl}_3\text{HgBr}$	165	C 3.10; 3.25; Cl 26.78; 26.60; Br 20.03; 20.23	C 3.03; Cl 26.68; Br 20.03
$\text{CCl}_3\text{HgBr} \cdot \text{C}_6\text{H}_5\text{N}$	87	C 15.15; 14.91; H 0.87; 0.81; Cl 22.08; 22.00; Br 16.57; 16.55	C 15.07; H 1.05; Cl 22.25; Br 16.72
$\text{CCl}_3\text{HgI}$	117	C 2.85; 2.93; Cl 23.42; 23.92	C 2.69; Cl 23.85
$\text{CCl}_3\text{HgCl}$	173	C 3.29; 3.16; Hg 56.90	C 3.39; Hg 56.60
$\text{CCl}_3\text{HgOH}$	175	C 3.91; 4.00; H 0.02; 0.05; Cl 31.66	C 3.57; H 0.30; Cl 31.65
$\text{CCl}_3\text{HgC}_6\text{H}_5$	116	C 20.84; 21.02; H 1.13; 1.22; Cl 26.11; 26.43	C 21.23; H 1.27; Cl 26.79
$\text{CHCl}_3\text{HgBr}$	152	C 3.36; 3.24; H 0.23; 0.28; halide 40.98	C 3.30; H 0.28; halide 41.39
$\text{CHCl}_3\text{HgI}$	130	C 2.49; 2.59; H 0.32; 0.31	C 2.92; H 0.24
$\text{CCl}_2=\text{CHCH}_2\text{HgI}$	46	C 8.80; 8.85; H 0.72; 0.64; Cl 16.97; 17.04	C 8.23; H 0.69; Cl 16.20
$\text{CCl}_2=\text{CHCH}_2\text{HgBr}$	94.5	C 8.67; 8.73; H 0.79; 0.77	C 9.23; H 0.77
$\text{CCl}_2=\text{CHCH}_2\text{HgCl}$	100	C 10.17; 10.39; H 0.94; 1.13	C 10.41; H 0.87
$\text{C}_6\text{H}_5\text{HgOCOCCL}_3$	240	C 21.46; 21.43; H 1.10; 1.27; Hg 45.52; 46.05	C 21.60; H 1.15; Hg 45.35
$\text{CCl}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{HgI}^*$	101	C 10.65; 10.78; H 1.02; 0.98	C 10.64; H 1.12
$\text{CCl}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{HgBr}$	109	Br 20.30; 20.43	Br 19.75
$\text{CCl}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{HgCl}$	127	Cl 29.69; 29.56	Cl 29.54

\* Prepared from 1,1-dichloro-2-methyl-3-iodo-1-propene, b. p.  $77^\circ/10$  mm.

Found %: C 19.49; 19.49; H 2.05; 2.02 Calculated %: C 19.15; H 2.01

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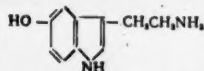
\*\* In Russian.



## SYNTHESIS OF DERIVATIVES OF 5-METHOXYINDOLE

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and M. N. Preobrazhenskaya

Derivatives of 5-hydroxyindole, a substance structurally related to serotonin,



which possesses diverse physiological properties, are of considerable interest, since many of them are stronger antimetabolites than serotonin.

In the present work, we synthesized a number of 2-aryl-5-methoxyindoles by condensation of *p*-anisidine with substituted  $\omega$ -haloacetophenones.

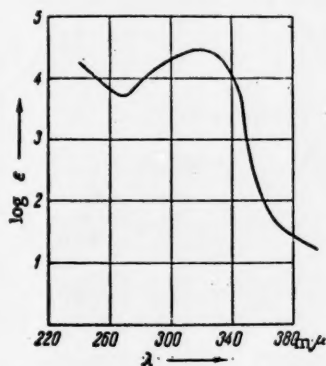


Fig. 1. Absorption spectrum of 2-phenyl-5-methoxyindole (I)

There is mention in the literature of the preparation by such a route of 2-phenyl-5-methoxyindole (I) [1] and 2-(*p*-methoxyphenyl)-5-methoxyindole (II) [2]; however, the experimental details, particularly those relative to the isolation of the reaction products (which is the greatest difficulty), were not reported.

The structure of the 2-phenyl-5-methoxyindole was proved [1] by ozonation to *N*-benzoyl-5-methoxyanthranilic acid [1]. The 2-(*p*-methoxyphenyl)-5-methoxyindole was also obtained from *p*-methoxyacetophenone *p*-methoxyphenylhydrazone [3], a compound which is extremely unstable to the action of light and air.

The yields and properties of the compounds prepared by us are presented in Table 1.

The ultraviolet absorption spectra for the indole preparations were all similar (see Table 2 and Figure 1).

The spectra were taken on an SF-4 spectrophotometer. In all cases, methyl alcohol was used as the solvent. In view of the poor solubility of II and VIII in methyl alcohol, the per cent absorption was determined for these substances (saturated solution, cell thickness 0.0113 cm).

3-(*p*-Methoxyphenyl)-5-Methoxyindole (XII) was prepared by cyclization of (*p*-methoxyphenyl)-aminomethyl-(*p*-methoxyphenyl)-ketone [*p*-methoxy- $\alpha$ -(*p*-methoxyanilino) acetophenone] (XIII) by means of zinc chloride.

The ultraviolet absorption spectra for the original anisidine ketone (XIII), 2-(*p*-methoxyphenyl)-5-methoxyindole (II), and 3-(*p*-methoxyphenyl)-5-methoxyindole (XII) differed sharply (see Figure 2).

Janetzky and Verkade [4] prepared 2-phenylindole in 39% yield by the action of zinc chloride on phenacylaniline at a temperature of 180°. The authors assumed that the initially formed 3-phenylindole rearranged to 2-phenylindole under the influence of the zinc chloride at the high temperature. The rearrangement of 3-phenylindole to 2-phenylindole by heating with zinc chloride at 180° had been carried out earlier by Fischer

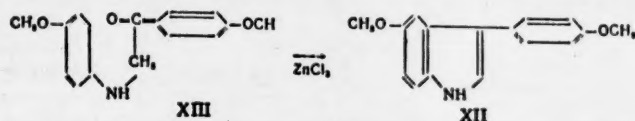
TABLE I

Formula No.	Original haloacetophenone	$\text{CH}_3\text{O}-\text{C}_6\text{H}_3(\text{NH})-\text{R}$	Yield	M.p. °C	Found, %			Calculated, %		
					C	H	N	C	H	N
I	$\text{C}_6\text{H}_5\text{COCH}_2\text{Br}$	$-\text{C}_6\text{H}_5$	50	167–167.5° 170(°)						
II	$4\text{-CH}_3\text{OC}_6\text{H}_4\text{COCH}_2\text{Br}$	$-\text{C}_6\text{H}_4\text{OCH}_3$ (4)	28	214.5–215.5° 213–214(°) 215(°)						
III	$4\text{-CH}_3\text{C}_6\text{H}_4\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_4\text{CH}_3$ (4)	50	185–185.5	80.96	6.60	5.95	80.98	6.37	5.90
IV	$2,5\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_3(\text{CH}_3)_2$ (2,5)	23	174–175	81.23	6.76		81.24	6.82	
V	$3,4\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{COCH}_2\text{Br}$	$-\text{C}_6\text{H}_3(\text{CH}_3)_2$ (3,4)	24	146–147	81.12	6.94	5.63	81.24	6.82	5.73
VI	$4\text{-BrC}_6\text{H}_4\text{COCH}_2\text{Br}$	$-\text{C}_6\text{H}_3\text{Br}$ (4)	66	200–201	58.54	4.10	4.68	59.61	4.00	4.64
VII	$4\text{-ClC}_6\text{H}_4\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_4\text{Cl}$ (4)	83	190.5–191	70.21	4.66	5.33	69.91	4.69	5.43
VIII	$4\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (4)	98	295–298	84.21	5.59	4.40	84.25	5.73	4.78
IX	$4\text{-CH}_3\text{CONHC}_6\text{H}_4\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_4\text{NHCOCCH}_3$ (4)	18	267.5–269	72.79	5.74		72.87	5.75	
X	$4\text{-HOC}_6\text{H}_4\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_4\text{OH}$ (4)	10	206–207	74.82	5.76		75.29	5.47	
XI	$2\text{-HOC}_6\text{H}_4\text{COCH}_2\text{Cl}$	$-\text{C}_6\text{H}_4\text{OH}$ (2)	8.5	162.5–163.5	75.39	5.46	5.90	75.92	5.47	5.85

• Above line – our data; below line – literature data.



and Schmitt [5]. We successfully showed that the substituted 3-phenylindole (XII) was actually formed under the milder conditions (in ethyl alcohol) of the cyclization of anisidinoketone (XIII).



The spectra were taken in the laboratory of L. A. Kazitsina. We consider it our duty to express to her our appreciation.

TABLE 2

R	$\lambda_{\max}$	$\log \epsilon_{\max}$
I -	318	4.43
II -		
III -	319	4.50
V -	320	4.50
VII -	323	4.54
XI -	326	4.47
IX -	326	4.54
VIII -	334	

## EXPERIMENTAL

**I** The 2-aryl-5-methoxyindoles were prepared by the following method: a mixture of 5 moles of p-anisidine and 1 mole of the  $\omega$ -haloacetophenone was heated for 15 minutes at 180-200°. The cooled reaction mixture was dissolved in the minimum amount of methyl alcohol and poured into approximately a ten-fold volume of hydrochloric acid (1:4). The resulting precipitate was dried in a vacuum desiccator over calcium chloride.

The 2-phenyl-5-methoxyindole (I) was crystallized from methyl alcohol.

The 2-(p-methoxyphenyl)-5-methoxyindole (II) and also the 2-(p-bromophenyl)-5-methoxyindole (VI) were purified by crystallization from carbon tetrachloride and then from methyl alcohol.

The 2-(p-chlorophenyl)-5-methoxyindole (VII) was crystallized from carbon tetrachloride and then from ethyl alcohol.

The 2-(p-tolyl)-5-methoxyindole (III) was crystallized from a mixture of benzene and isooctane and then from benzene.

The 2-(p-xylyl)-5-methoxyindole (IV) was extracted with isooctane, and, after elimination of the solvent, it was crystallized from methyl alcohol.

The 2-(o-xylyl)-5-methoxyindole (V) was extracted with ether, the ether solution was purified by boiling with  $Al_2O_3$ , and, after elimination of the ether, the material was treated with benzene-isooctane mixture. The resulting material was crystallized from benzene and then from aqueous methyl alcohol.

The 2-(p-diphenyl)-5-methoxyindole (VIII) was crystallized from toluene.

The 2-(p-acetamidophenyl)-5-methoxyindole (IX) was crystallized from acetic acid and then from methyl alcohol.

The 2-(p-hydroxyphenyl)-5-methoxyindole (X) was extracted with isooctane and, after removal of the solvent, crystallized from benzene.

The 2-(o-hydroxyphenyl)-5-methoxyindole (XI) was extracted with benzene, the solution boiled with  $Al_2O_3$ , and, after evaporation of the solvent, crystallized from benzene-isooctane mixture.

**II** Preparation of (p-methoxyphenyl)-aminomethyl-(p-methoxyphenyl)-ketone (XIII). 9.84 g of p-anisidine was added to a solution of 9.16 g of p-methoxy- $\omega$ -bromoacetophenone in 30 ml of ethyl alcohol. After

half an hour, the precipitated anisidino ketone was suction filtered. Some additional amount of anisidino ketone was obtained by evaporation of the mother liquor. The overall yield was 9.5 g (88%). M. p. 126-127° (from alcohol).

Found %: N 5.11  $C_{16}H_{17}O_3N$ . Calculated %: N 5.16

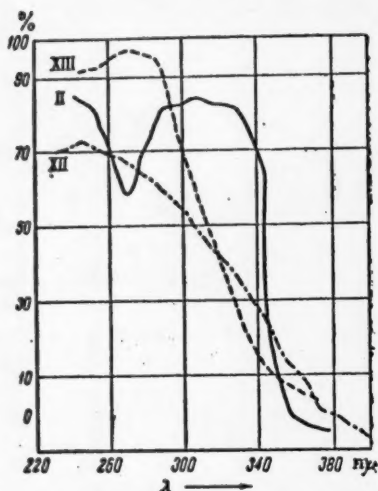


Fig. 2. Absorption spectra of 2-(p-methoxyphenyl)-5-methoxyindole (II), 3-(p-methoxyphenyl)-5-methoxyindole (XII), and (p-methoxyphenyl)-aminomethyl-(p-methoxyphenyl)-ketone (XIII). Saturated solutions,  $d = 0.0113$  cm.

**III. Preparation of 3-(p-methoxyphenyl)-5-methoxyindole (XII).** 5 g of (p-methoxyphenyl) aminomethyl-(p-methoxyphenyl)-ketone and 10 g of zinc chloride were dissolved in 20 ml of absolute alcohol and heated to boiling 7 hours. The reaction mixture was poured into 150 ml of hydrochloric acid (1:4). The resulting precipitate was dried in a vacuum desiccator over calcium chloride, and the indole was extracted from it with isooctane. 1.1 g (23%) of 3-(p-methoxyphenyl)-5-methoxyindole was obtained, and this was recrystallized from methyl alcohol, m. p. 151.5-152°.

Found %: C 75.94; 75.52; H 6.39; 6.16; N 5.75  $C_{16}H_{15}O_2N$ . Calculated %: C 75.86; H 5.97; N 5.53.

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## A STUDY OF THE REACTION BETWEEN AMMONIA AND ZINC CHLORIDE IN AQUEOUS MEDIUM

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and R. S. Mikhitarian

A study of the reaction between zinc chloride and ammonia in aqueous medium over the entire range of concentration of the latter in solution at different temperatures has not been carried out. There are investigations devoted to the synthesis of zinc chloride ammoniates and their thermal stability.

Anhydrous hexamminozinc chloride has been prepared by passing gaseous ammonia through anhydrous zinc chloride [1, 4]. The dissociation pressure of hexamminozinc chloride and the products of its decomposition have been determined [2, 4]. Monoaquopentamminozinc chloride has been prepared by cooling a saturated ammoniacal solution of zinc chloride [11]. Tetramminozinc chloride with various water contents has been obtained by cooling an ammoniacal solution of zinc chloride [3, 5, 7]. The decomposition temperature has been determined [3]. Diamminozinc chloride, both anhydrous and with water of crystallization, has been prepared by various methods: by dissolving zinc oxide in solutions of ammonium chloride [9], by passing gaseous ammonia through a solution of zinc chloride [5, 8], by the thermal decomposition of higher ammoniates of zinc chloride [5, 6], etc. The dissociation temperature and the temperature of incipient decomposition of diamminozinc chloride have been determined [1, 3]. Monoamminozinc chloride is the final product of the thermal decomposition of the higher ammoniates, and it can be distilled without decomposition [5]. Andre [8] and Allean [10] indicated the preparation of ammonia-containing basic salts. They prepared ammonia-containing basic salts by dissolving anhydrous zinc chloride in concentrated aqueous solutions of ammonia.

### EXPERIMENTAL

The study of the reaction between zinc chloride and ammonia in aqueous medium was carried out by the isothermal solubility method. The reaction between ammonia and zinc chloride in aqueous medium proceeds in two stages: at low concentrations of ammonia in the equilibrium liquid phase ammonia-containing basic salts crystallize out, and with high concentrations zinc chloride ammoniates crystallize.

The region of crystallization of ammoniates was considered as a ternary system composed of zinc chloride, ammonia, and water, and it was studied at two temperatures - 0 and 25° - with the aim of determining the change in solubility of zinc chloride in aqueous-ammoniacal solutions and the compositions of the crystallized phases in relation to temperature. The region of crystallization of the basic salts was studied only at 25°.

In the region of crystallization of basic salts, crystalline zinc chloride was introduced into aqueous solutions of ammonia of various concentrations until precipitates of basic salts appeared. In studying the region of crystallization of the ammoniates, gaseous ammonia was passed through solutions of zinc chloride of various concentrations until a crystalline precipitate appeared.

The mixtures prepared in the region of crystallization of ammoniates were held in closed vessels in a constant-temperature bath for 6-8 hours, while for mixtures in the region of crystallization of basic salts the time required for establishment of equilibrium between the liquid and solid phases was 20-25 days.

The liquid and solid phases of both regions of the system were analyzed for  $Zn^{2+}$  content by precipitation with disubstituted ammonium phosphate, for  $Cl^-$  by titration with silver nitrate solution, for  $OH^-$  and  $NH_3$  in both the solid and liquid phases, by direct titration with sulfuric acid.

## DISCUSSION OF RESULTS.

Crystallization of ammonia-containing basic salts was complete at contents of 9.04 weight % ammonia and 18.92 weight % zinc chloride in the equilibrium liquid phase. The content of zinc chloride increased with an increase in the concentration of ammonia, and was directly proportional to its content in the liquid phase (Figure 2).

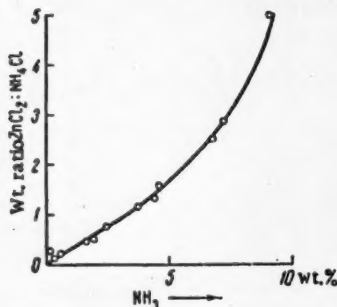


Fig. 1

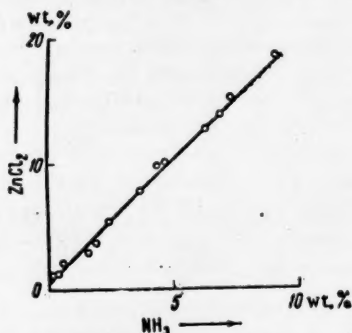


Fig. 2

The crystallization of ammonia-containing basic salts of zinc chloride was the result of the partial proceeding of an exchange reaction between ammonium hydroxide and zinc chloride. With an increase in the concentration of ammonia in the liquid phase, the exchange between the indicated substances decreased parabolically (Figure 1).

The solid phases in the region of crystallization of basic salts of zinc chloride were of variable composition. All of them, without exception, contained ammonia and had the composition  $\text{ZnCl}_2 \cdot n\text{Zn}(\text{OH})_2 \cdot s\text{NH}_3 \cdot x\text{H}_2\text{O}$ , where the coefficients  $n$ ,  $s$ , and  $x$  have different values, both integral and fractional.

The content of ammonia in the solid phases depended on its concentrations in the liquid phases. The more ammonia in the liquid phase, the more it entered into the composition of the solid phase, and the content of zinc hydroxide was thereby correspondingly decreased.

The ammonia-containing basic salts of zinc chloride, in spite of the different chemical compositions, possessed identical properties (thermal, crystalloptical, etc.). Debye crystallograms indicated the salts to be identical. Correspondence of the several properties and also of the crystal lattices of the ammonia-containing basic salts is probably connected with isomorphic substitution of the groups entering into the composition of these substances, particularly  $\text{OH}^-$  and  $\text{NH}_3$ , and, perhaps,  $\text{H}_2\text{O}$  and  $\text{NH}_3$ .

Crystallization of the ammoniates, both at  $0^\circ$  and at  $25^\circ$ , began at contents of 11.0 weight % ammonia and 28.0 weight % zinc chloride in the equilibrium solutions. Between the beginning of crystallization of the ammoniates and the conclusion of crystallization of the ammonia-containing basic salts there was a certain interval (from 9.0 to 11 weight % ammonia in solution) in which, owing to the high solubility of the newly formed compounds, crystallization of the solid phase did not take place. The system consisted only of an homogeneous liquid phase. In the region of crystallization of ammoniates at  $0^\circ$ , two compounds crystallized:  $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ . The experimental results from the study of the solubility of zinc chloride in aqueous-ammoniacal solutions in the region of crystallization of ammoniates at  $0^\circ$  are presented in Figure 3, while those obtained at  $25^\circ$  are presented in Figure 4. Two compounds also crystallized at  $25^\circ$  in the region of the crystallization of ammoniates in the system  $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.35\text{H}_2\text{O}$ .

The compositions of the above-indicated substances were established by the method of residues and chemical analysis. The crystallization of  $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$  both at  $0^\circ$  and at  $25^\circ$ , began at an ammonia content of 11 weight % and ended at 24.64 weight % ammonia in the equilibrium solution.

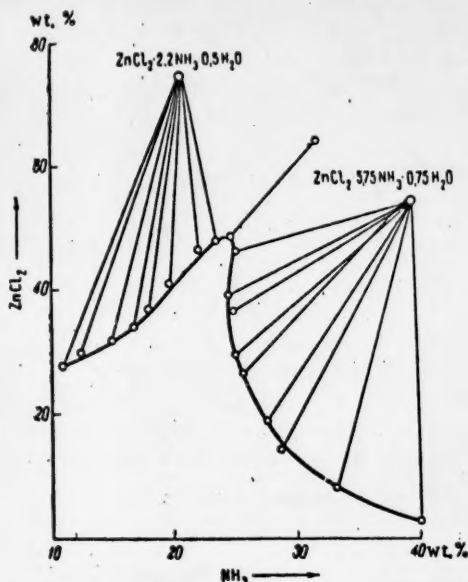


Fig. 3

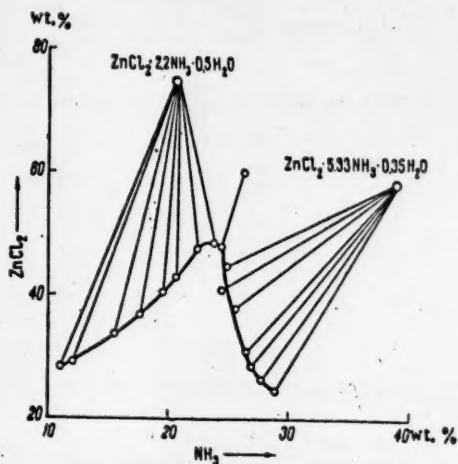


Fig. 4

The solubility of the latter compound increased with the concentration of ammonia in the solution, and did not depend on temperature. Therefore, the solubility of zinc chloride at 25° coincides with that at 0°. The point of cocrystallization of  $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$  and 0°;  $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.35\text{H}_2\text{O}$  at 25° corresponds to a solution composition of  $\text{NH}_3$  24.14 weight %,  $\text{ZnCl}_2$  48.38 weight %, and  $\text{H}_2\text{O}$  26.98 weight %.

Salting out of the higher ammoniates  $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.35\text{H}_2\text{O}$  proceeds several times more rapidly at the beginning of crystallization than at the end; this was particularly clearly noticeable at 0°. Lowering of the temperature promoted crystallization of substances rich in ammonia and water of crystallization. The enumerated zinc chloride ammoniates were well crystallized substances. In air, all of them, without exception, decomposed. After 2.5-3 hours in air,  $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$  was converted to anhydrous diamminozinc chloride,  $\text{ZnCl}_2 \cdot 2\text{NH}_3$ . The substances  $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ , and  $\text{ZnCl}_2 \cdot 5.33\text{NH}_3 \cdot 0.35\text{H}_2\text{O}$  both in air and over 96% sulfuric acid, were also converted in 5-6 hours to anhydrous diamminozinc chloride.

There were three endothermic effects in the heating curve of  $\text{ZnCl}_2 \cdot 2.2\text{NH}_3 \cdot 0.5\text{H}_2\text{O}$ . 0.2 mole of ammonia and all of the water of crystallization were liberated at the first two thermal effects at 65° and 125°. At the third thermal effect, 230-245°, the anhydrous diamminozinc chloride, which remained, melted and began its decomposition. Further heating of the diamminozinc chloride was not accompanied by thermal effects. In the present case, it was impossible to establish by means of heating curves the temperature of the decomposition of diamminozinc chloride to monoamminozinc chloride. At high temperatures - above 400° - the monoamminozinc chloride partially sublimed. There were two endothermic effects on the heating curve of  $\text{ZnCl}_2 \cdot 5.75\text{NH}_3 \cdot 0.75\text{H}_2\text{O}$ . At the first effect, 75-100°, water and ammonia were simultaneously eliminated to produce anhydrous diamminozinc chloride. The second, at 230-245°, corresponded to melting and the beginning of decomposition of  $\text{ZnCl}_2 \cdot 2\text{NH}_3$ . Thus, zinc chloride ammoniates containing more than two molecules of ammonia are unstable compounds which readily give up ammonia and water, both on heating and at room temperature.



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## THE CATALYTIC DEHYDRATION OF ALCOHOLS OVER ANHYDROUS MAGNESIUM SULFATE

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I. M. Khorlina and L. S. Konkova

Very little work has been carried out on the vapor phase dehydration of alcohols over metallic sulfates. Senderens [1] studied the dehydration of ethanol over anhydrous calcium sulfate, and Zakharova [2] the dehydration of methylethylethynyl carbinol over magnesium sulfate [3].

The problem we set ourselves was the establishment of the conditions of employment of magnesium sulfate as a catalyst for the dehydration of alcohols. In the present work we studied the dehydration of the following secondary alcohols 2-propanol, 2-pentanol, cyclopentanol and cyclohexanol. We showed that these alcohols are substantially completely dehydrated when passed over anhydrous magnesium sulfate at 400-410° with a space velocity of 0.4. Special attention was paid to the dehydration of cyclohexanol. It was established that cyclohexene is the sole product of the reaction. Products of dehydrogenation and isomerization are absent, and the catalyst does not lose its activity after use for 500 hours and does not require regeneration. Operation, however, of the process of dehydration of cyclohexanol for a longer period at lower temperatures of the order of 270-330° caused the catalyst to gradually lose activity, the yield of cyclohexene being sharply reduced after the 80th to the 105th hour of operation (Fig. 1).

We attribute this change in behavior to the hydration of the catalyst with water released during the reaction. The magnesium sulfate becomes progressively hydrated in our experiments and the whole of its surface is gradually covered with water.

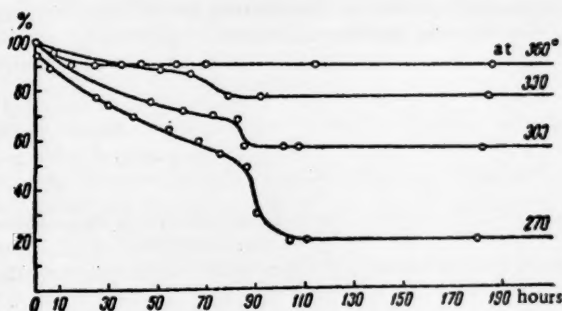


Fig. 1

Sizo Hirano [4] reports the temperatures of transformation of one magnesium sulfate into the other ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  into  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ). According to the authors' data the transformation of  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  into  $\text{MgSO}_4$  occurs at 200-300°.

Berg and Nikolaev [5] found that magnesium sulfate loses the last molecule of water in an atmosphere of water vapor at 340-360-370°; during dehydration in air the last molecule of water starts to come off at about 280°.

On the basis of these facts we may suggest that in our experiments at temperatures below 360-370° the magnesium sulfate apparently has the mixed composition of  $\text{MgSO}_4 \cdot \text{H}_2\text{O} - \text{MgSO}_4$ ; the latter must have a lower catalytic activity than anhydrous magnesium sulfate which is only formed at a temperature above 370°.

This suggestion is confirmed by our observation that the catalyst reached a maximum and constant activity at 380-400°.

The influence of other factors, in particular the change of shape and area of the surface, is evidently less pronounced. We found that the surface area (determined by the absolute method with benzene) remains substantially unchanged even after prolonged use of the catalyst.

A study was also made of the kinetics of dehydration of cyclohexanol, cyclopentanol, 2-propanol and 2-pentanol over magnesium sulfate. The values of the apparent activation energies were calculated and found to be fairly similar in all cases. This indicates that a similar dehydration mechanism is involved for all the alcohols examined and that the molecule of the alcohol has its hydroxyl group oriented towards the surface of the catalyst.

#### EXPERIMENTAL

The work was carried out with a flow type of apparatus in a horizontal tubular furnace fitted with an automatic feed device.

The catalyst was prepared in the following way: magnesium sulfate was put into the catalytic tube and slowly heated in a stream of dry air. Appreciable evolution of water commenced at 100°. The greatest amount of water came off at 150-160°. This temperature was maintained until water ceased to come off, after which it was gradually raised to 300°; a further (very small) amount of water then came off. No further loss of water was observed on raising the temperature to 400°.

All the experiments were performed over a 30 ml bed of previously dehydrated magnesium sulfate.

The following substances were used: cyclohexanol with b.p. 160°/750 mm,  $n_D^{20}$  1.4640,  $d_4^{20}$  0.9460; cyclopentanol (prepared by hydrogenation of cyclopentanone at 50° and a hydrogen pressure of 200 atm. over Raney nickel) with b.p. 141°/758 mm,  $n_D^{20}$  1.4520,  $d_4^{20}$  0.9469; 2-propanol with b.p. 82°/755 mm,  $n_D^{20}$  1.3778,  $d_4^{20}$  0.7888; and 2-pentanol (prepared from n-propyl bromide and acetaldehyde by the Grignard reaction) with b.p. 116-117°/744 mm,  $n_D^{20}$  1.4000 and  $d_4^{20}$  0.8087.

The yield of propylene was determined by analysis of the gases in an All-Union Thermotechnical Institute apparatus. Yields of cyclohexene, cyclopentene and pentene were determined by fractional distillation of the catalyzates or by titrimetric determination of the bromine numbers by Kaufmann's method. Both methods gave concordant results. All yields were calculated on the basis of the alcohols taken into reaction.

A series of experiments was run at 270, 300, 330 and 360° in order to calculate the relation between the activity of the catalyst and the period of its utilization. Cyclohexanol was admitted at a space velocity of 0.4. Experiments were run at each temperature for 190 hours over the same portion of catalyst; the activity of the catalyst declined gradually (Fig.1).

The causes of loss of catalytic activity were investigated by observations on two specimens of catalyst: one freshly prepared and the other after being used for 80 hours. With the aid of a quartz torsion balance, adsorption isotherms of benzene vapor were plotted at 0°. The specific surface was then calculated and was found to be substantially the same for both specimens. Its magnitude did not exceed 20 m<sup>2</sup>/g.

A very small number of narrow pores, present in the freshly prepared specimen, disappear after prolonged utilization of the catalyst.

The data indicate that the decrease of activity after prolonged operation is not caused by a change of catalyst structure. The optimum conditions of dehydration of cyclohexanol, cyclopentanol and 2-propanol were established by varying the experimental temperature and the space velocity of the alcohols. Each experiment was performed over a fresh portion of catalyst. Results are presented in Table 1.

TABLE 1

Experimental temperature °C	Cyclohexene		Cyclopentene		Propylene		
	Space velocities of alcohols						
	0.2	0.4*	0.6	0.2	0.4	0.2	0.4
350	86.0	88.0	78.0	65.0	75.0	73.0	70.0
360	90.0	90.0	83.0	72.5	80.5	76.0	74.0
370	92.5	92.0	86.0	77.0	81.0	82.0	75.0
380	95.0	95.0	86.0	80.0	83.0	88.0	76.0
390	98.0	98.0	86.0	87.0	86.0	94.0	82.5
400	100.0	100.0	86.0	92.0	93.0	100.0	88.4
410	—	—	86.0	96.0	98.0	98.0	88.0
420	—	—	—	100.0	100.0	95.6	84.5

\* At 205° the yield is 44%; at 250° it is 79%.

The cyclohexene obtained had constants identical with those given in the literature (b.p. 81-82°/758 mm,  $n_D^{20}$  1.4470,  $d_4^{20}$  0.8111), and did not contain the product of isomerization (methylcyclopentene) as shown by the spectroscopic data.

Spectrum of product of dehydration of cyclohexanol: 276 (2.5); 395 (7); 455 (1.5); 495 (2); 641 (1.5); 823 (80); 875 (2.5); 904 (3); 963 (2.5); 1020 (0); 1038 (3); 1068 (4.5); 1117 (0); 1144 (2,b,d); 1223 (12); 1243 (3); 1267 (6); 1296 (0); 1342 (2); 1352 (1.5); 1377 (0); 1432 (10); 1443 (4); 1545 (0); 1593 (0.5) 1652 (25).

The cyclopentene obtained by dehydration of cyclopentanol had b.p. 43°,  $n_D^{20}$  1.4228 and  $d_4^{20}$  0.7791.

The apparent activation energy of dehydration was determined for cyclohexanol, cyclopentanol, 2-pentanol and 2-propanol. This series of experiments was carried out at temperatures of 360-400° with a constant space velocity of the alcohols of 0.4. The kinetic experiments with cyclohexanol and 2-propanol were performed over 1 ml of catalyst, those with cyclopentanol and 2-pentanol over 3 ml. The degree of conversion of the alcohols did not exceed 25-30%. In the present case the degree of conversion can be equated without serious error with the velocity constant of the reaction, and the activation energy can then be determined (using the Arrhenius equation) from the dependence of the degree of conversion (ln %) on the temperature. Results of this series of experiments are detailed in Table 2 which shows the similarity between the apparent energies of activation of the individual alcohols. This can be attributed to the identical orientation of the alcohol molecules to the surface of the catalyst. The small differences between the magnitudes of the activation energies can then be accounted for by the influence of different substituents. A possible alternative explanation is that the rate-determining step in the dehydration of the alcohols is the desorption of the water formed during the reaction. The question as to which of these two effects is manifested during dehydration over magnesium sulfate is of interest in itself and will be the subject of further investigation.

An additional series of experiments was run with cyclohexanol at lower temperatures (260-350°) with the objective of ascertaining the effect of the presence of  $MgSO_4 \cdot H_2O$  on the activation energy. An activation energy of 18,200 cal/mole was found. The intermediate hydrates of magnesium sulfate formed by reaction with water are evidently stable at low temperatures and hinder the dehydration of cyclohexanol.

Our investigation has thus demonstrated the possibility of using anhydrous magnesium sulfate as a catalyst for dehydration of the secondary alcohols: cyclohexanol, cyclopentanol, pentanol-2 and propanol-2. Dehydration of these alcohols goes substantially to completion at a temperature of about 400° and with a flow rate of the alcohols of 0.2-0.4.

Anhydrous magnesium sulfate retains its catalytic activity after use for over 500 hours at a temperature of 400°, and it does not require regeneration. Magnesium sulfate does not promote isomerization of the ring during dehydration of cyclohexanol.

TABLE 2

Alcohol	% yield of olefins					Apparent activation energy
	at 360°	at 370°	at 380°	at 390°	at 400°	
Cyclohexanol	16.6	17.7	22.1	29.4	32.4	14.980
Cyclopentanol	15.12	17.8	21.12	23.15	25.4	14.370
2-Pentanol*	16.8	18.0	25.5	26.1	28.9	15.190
2-Propanol	13.5	18.8	21.3	28.0	31.68	14.760

\* The pentene isolated had b.p. 35-37°,  $n_D^{20}$  1.3807 and  $d_4^{20}$  0.6512.

The calculated values of the apparent activation energies of dehydration of cyclohexanol, cyclopentanol, 2-pentanol and 2-propanol are close to one another. This indicates that the molecules of the alcohols are identically oriented with their hydroxyl groups towards the surface of the catalyst.

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# NITRATION OF AROMATIC COMPOUNDS WITH NITROGEN PENTOXIDE BY A RADICAL MECHANISM

A. N. Baryshnikova and A.I. Titov

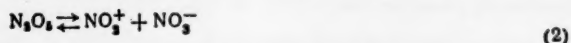
(Presented by Academician A.V. Topchiev, January 23, 1957)

We were first to describe the nitration of unsaturated and aromatic compounds by a radical mechanism, using nitrogen dioxide, in 1941 [1]; these investigations were developed in the years 1945-1953 [2-7]. They showed that the initial determining step in the reaction is the addition of the monomer of nitrogen dioxide  $\text{NO}_2$  at the  $\pi$ -bond, leading ultimately to formation of a radical

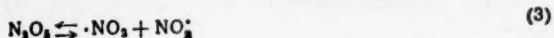


Transformations of the resultant  $\text{Ar} \begin{array}{c} \text{H} \\ \diagup \\ \text{NO}_2 \end{array}$  radical with  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$  and  $\text{O}_2$  lead to diverse products. For example in the case of benzene [5,5] the products are nitrobenzene, p- and m-dinitrobenzene (up to 30%), symm. trinitrobenzene (up to 30%), nitrophenols (up to 30%), and others; chlorobenzene gives many nitro derivatives of m-chlorophenol, etc. in addition to other products. The predominating formation of anomalous products (polynitro compounds and nitrophenols) is characteristic of nitration by a radical mechanism.

The possibility of nitration by a radical mechanism with nitrogen pentoxide came to light when, apart from its ionic breakdown [1]



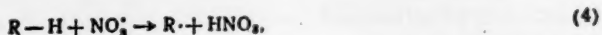
we suggested [7,8] that  $\text{N}_2\text{O}_5$  might dissociate to a radical-like dioxide and nitrogen trioxide



Subsequently we showed that this process took place.

The concepts of the radical dissociation of nitrogen pentoxide enabled methods to be found for controlling its rapid reaction with paraffins and for establishing a series of special features of this type of nitration, in particular its inhibition by traces of nitrogen dioxide [8].

The remarkably high activity of nitrogen trioxide  $\text{NO}_3$  in reactions with paraffins (even at low temperatures)

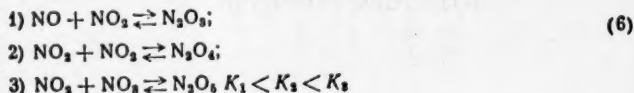


In comparison with the activity of  $\text{NO}$  and  $\text{NO}_2$  is explained by the strongly electrophilic character and the high degree of unsaturation of the unpaired electron of the oxygen of  $\text{O} \cdot \text{N}-\text{O} \cdot$ . We may assume that the electrophilicity of these oxides will be proportional to the electrolytic dissociation constants of hyponitrous, nitrous and



$$K_{\text{HNO}_2} > K_{\text{HNO}_3} > K_{\text{HNO}}, \quad (5)$$

and that the degree of their unsaturation will be proportional to the constants of their equilibrium with  $\text{NO}_2$ .



On the basis of the considerations developed above, we should expect a very high activity of nitrogen pentoxide in comparison with nitrogen dioxide during nitration of aromatic compounds by a radical mechanism. Due, however, to the extremely rapid nitration of aromatic compounds by  $\text{N}_2\text{O}_5$  under ordinary conditions by an ionic mechanism, relatively little product is formed by the radical reaction.

Nitration by a predominantly radical mechanism was carried out by conducting the process at high temperature in a nonpolar medium that facilitated dissociation of  $\text{N}_2\text{O}_5$  according to equation (3) and suppressed the development of a nitronium cation according to scheme (2). The predominance of anomalous compounds (polynitro derivatives and nitrophenols) among the reaction products, in spite of the enormous excess of the original aromatic compound, is evidence of interaction of nitrogen pentoxide by a radical mechanism. Data for some experiments are presented below.

I. A solution of 5 g nitrogen pentoxide in 50 ml carbon tetrachloride was added dropwise to 200 g benzene at a bath temperature of  $70^\circ$  over a period of 40 minutes. After part of the reaction mass had been distilled in vacuum, it was worked up by the previously described method [5].

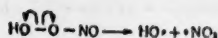
Extraction with sodium carbonate gave 0.9 g of a mixture of nitrophenols consisting mainly of 2,4-dinitrophenol; from this mixture, as well as from the extracts with caustic alkali solution, 0.1 g o-nitrophenol was obtained (in each case) by careful steam distillation. From the neutral residue was isolated 1.25 g nitrobenzene and 1.21 of a mixture of dinitrobenzenes consisting mainly of p- and m-dinitrobenzenes; the p-isomer was separated in a fairly pure form (m.p.  $163-165^\circ$ ) after one recrystallization from alcohol. Performance of the reaction at  $0-20^\circ$  gave about 7.5 g nitrobenzene, 0.5 g of a mixture of dinitrobenzenes (mainly m-isomer) and only traces of nitrophenols.

II. A solution of 5 g nitrogen pentoxide in 50 ml  $\text{C}_2\text{H}_2\text{Cl}_4$  was added dropwise to 200 ml chlorobenzene at  $100^\circ$ . Working-up in a similar manner with sodium carbonate solution gave 1.4 g of a liquid mixture of nitrochlorophenols; reaction of the latter at  $100^\circ$  with nitric acid of s.g. 1.4 enabled crystalline trinitro-m-chlorophenol with m.p.  $106-107^\circ$  to be readily isolated. The neutral product of the reaction consisted of 1.2 g of a mixture of nitrochlorobenzenes and of a higher boiling residue. Similar results were obtained in the nitration of nitrobenzene.

III. Nitration of toluene with nitrogen pentoxide at elevated temperature gave, as in the reaction with  $\text{NO}_2$  [6, 8], mainly products of transformation in the side chain (phenylnitromethane, ethers of benzyl alcohol, benzaldehyde) and mononitrotoluenes with a small admixture of dinitro derivatives. Reaction at the ordinary or at reduced temperature led to formation almost exclusively of a mixture of mono- and dinitrotoluenes; very heavy dilution with toluene or a large admixture of pyridine promoted formation of dinitrotoluene (mainly 2,4-isomer). In the latter case the nitration proceeded essentially in an "alkaline medium".

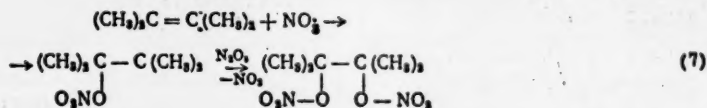
The results of nitration with nitrogen pentoxide by a radical mechanism are similar to those obtained in reaction with nitrogen dioxide. The main difference is that the reaction with the  $\text{NO}_3^\cdot$  formed by dissociation of  $\text{N}_2\text{O}_5$  goes many times faster, and even nitrobenzene can easily escape detection although the latter is perfectly stable to the action of  $\text{NO}_3$  after prolonged heating. The attack of  $\text{NO}_3^\cdot$  on toluene is primarily directed (for understandable reasons) to the  $\alpha$ -hydrogen. These results are also similar to those obtained in the reaction of aromatic compounds with pernitrous acid [10,11] which breaks down with formation of free hydroxyl whose chemical character resembles that of  $\text{NO}_3^\cdot$ .



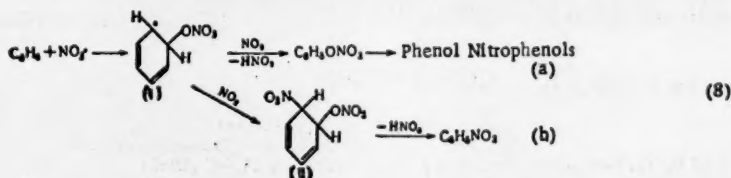


A considerable proportion of the normal mono- and dinitro derivatives (e.g. nitrobenzene and 2,4-dinitrotoluene) is probably formed by a purely ionic or latent ionic reaction with  $\text{NO}_2^+$  and  $\text{N}_2\text{O}_5$  respectively [1, 12].

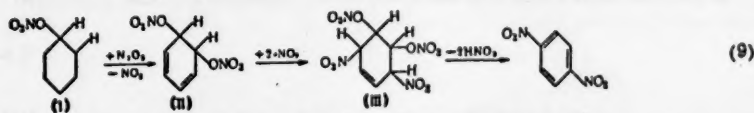
Radical nitration of unsaturated and aromatic compounds with nitrogen pentoxide undoubtedly commences with addition of  $\text{NO}_2$  at the  $\pi$ -bond. The simplest example of this type of reaction, observed by N. Ya. Demyanov [13, 14], is the formation of glycol dinitrate:



In the reactions that we investigated, the primary step is likewise the development of a radical of the type of (I) [see equation (8)]. Due to the great tendency towards aromatization, this radical is easily dehydrogenated by nitrogen dioxide (always present in the reaction sphere) to phenyl nitrate, and the latter is then naturally converted into phenol and its nitro derivatives (8, a). A reaction proceeding in parallel with the above is the addition of the monomer of nitrogen dioxide to radical (I) with formation of the adduct (II), and cleavage from the latter of the elements of nitric acid leads to formation of a mononitro derivative (8, b).

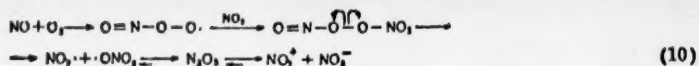


A more complex reaction is, for example, the formation of p-dinitrobenzene which may be represented by the following mechanism:

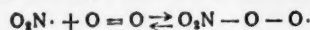


Radical (I), reacting with  $\text{N}_2\text{O}_5$  at the oxygen, forms the dinitrate (II); addition to it of two  $\text{NO}_2$  ions at the nitrogen in the 1,4-position gives the adduct (III), and cleavage from the latter of the elements of  $\text{HNO}_3$  leads to formation of p-dinitrobenzene.

It should be noted that the acceleration of the reaction of benzene [5] and other aromatic hydrocarbons (1) with oxides of nitrogen, previously observed by us, is bound up with the presence of oxygen due to partial development of  $\text{NO}_2^+$ ,  $\text{N}_2\text{O}_5$  and  $\text{NO}_2^+$ .



Participation of the  $\text{NO}_2$  radical in this reaction is also possible:



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\* The dissertation was presented for defence in 1941, but due to the wartime conditions it was defended in 1944.

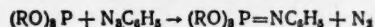
\*\* Original Russian pagination. See C.B. Translation.

\*\*\* In Russian.

## DIALKYLPHOSPHRYL-N-PHENYLTRIAZENES AND THEIR SALTS

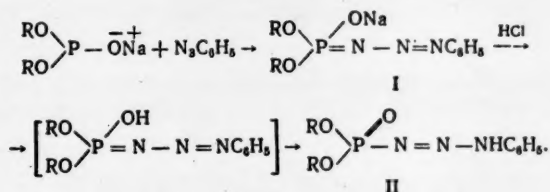
Corresponding Member of the Acad.Sci. USSR M.I. Kabachnik and  
V.A. Gilyarov

We have shown that full esters of acids of trivalent phosphorus enter into reaction with phenyl azide with formation of imidophosphates [1-3]:

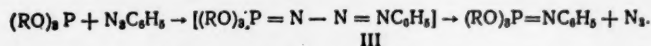


The reaction with phenyl azide was proposed for characterization of derivatives of acids of trivalent phosphorus [3].

It was a matter of interest to study this reaction with salts of dialkyl phosphites in which, judging by numerous data, the phosphorus is trivalent [4]. We found that free dialkyl phosphites do not react with phenyl azide; on the other hand, salts of dialkyl phosphites (triethylammonium and sodium salts) enter smoothly into reaction with formation of salts of dialkyl-N-phenylphosphoryl-triazenes (I), from which the free dialkylphosphoryl-N-phenyltriazenes (II) could be isolated; the latter are representatives of a new class of phosphorus-nitrogen compounds;



Formation of salts of triazenes in reactions of salts of dialkyl phosphites with phenyl azide can serve as confirmation of the previously advanced theory of the formation of triazenes III as intermediates in the reaction of trialkyl phosphites with phenyl azide [2].



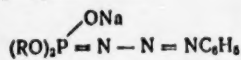
The reaction with phenyl azide takes place at an unshared electron pair of phosphorus; in this sense it is analogous to the reaction with sulfur. In the case of phenyl azide, however, the sodium salts react very much more rapidly than the triethylammonium salts. Such a difference is not observed in the reaction with sulfur [5].

The sodium salts of dialkyl phosphoryltriazenes are light yellow crystalline substances, not hydrolyzed by atmospheric moisture, soluble in some organic solvents and in water (the aqueous solutions break down on standing); on melting they decompose with loss of nitrogen. They probably possess the structure I in which the  $\text{Na}^+$  ion is at

the oxygen. Yields and constants of these salts are presented in Table 1.

TABLE 1

Sodium Salts of Dialkyl Phosphoryltriazenes



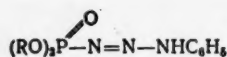
R	Yield (%)	M.p. °C (not corrected)	C, %		H, %		N, %	
			Found	Calc.	Found	Calc.	Found	Calc.
$\text{C}_2\text{H}_5$	62.8	147.5–148.5	43.08	43.02	5.51	5.41	15.24	15.05
			43.21		5.39		15.34	
$\text{C}_3\text{H}_7$	32.5	142.0–142.5	—	—	—	—	13.32	13.63
			—		—		13.32	
<i>n</i> - $\text{C}_4\text{H}_9$	47.8	142.0–143.0	—	—	—	—	14.14	13.63
			—		—		14.38	
$\text{C}_6\text{H}_5$	46.7	145.0–146.0	49.89	50.14	6.74	6.91	12.65	12.50
			49.87		6.51		12.61	

The free triazenes were isolated from the triethylammonium salts in vacuum (method A), and from the sodium salts by the action of hydrochloric acid in aqueous solution or of the calculated amount of acetic acid in ethereal solution (method B).

Yields, properties and results of analyses of dialkylphosphoryl-N-phenyltriazenes are presented in Table 2.

TABLE 2

Dialkylphosphoryltriazenes

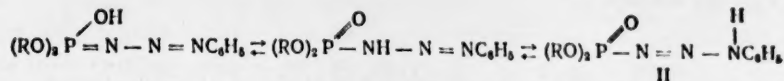


R	Method of synthesis	Yield, %	M.p. °C	C, %		H, %		P, %		N, %	
				Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$\text{CH}_3$	A	24.0	94.5—	41.90	41.93	5.39	5.24	13.41	13.54	17.89	18.34
			95.0	42.04		5.43		13.33		17.80	
			83.0—	46.96		6.32		11.61		16.21	
$\text{C}_2\text{H}_5$	A	38.8	83.5	47.02	46.70	6.23	6.22	11.39	12.07	16.18	16.34
			84.0—	—		—		—		—	
			85.0	—		—		—		—	
<i>n</i> - $\text{C}_4\text{H}_9$	A	17.5	64.0—	50.66	50.53	7.14	7.02	11.38	10.87	14.80	14.74
			65.0	50.61		7.08		10.98		14.92	
			—	53.52		7.75		9.38		—	
$\text{C}_6\text{H}_5$	B	90.0**	—	53.67	53.67	7.74	7.67	9.31	9.91	—	—
				—		—		—		—	

\* Calculated on the dialkyl phosphite.

\*\* Calculated on the sodium salt of the phosphoryltriazene.

Dimethyl-, diethyl- and diisopropylphosphoryl-N-phenyltriazenes are crystalline substances which break down when melted and give off nitrogen. They are soluble in the majority of organic solvents and insoluble in water. The structure of the dialkylphosphoryl-N-phenyltriazenes probably corresponds to formula II, since of the possible tautomeric forms:



the substance with formula II must possess the lowest acidity, and consequently the equilibrium must be shifted in the direction of this form [6]. These substances do not possess basic properties (do not form picrates or hydrochlorides) and thereby differ markedly from triazenes of the type of  $RN=N-NHAR$ .

Concerning the acidic properties, the dialkylphosphoryl-N-phenyltriazenes are soluble in solutions of caustic alkalis and form salts identical with the salts I obtained from dialkyl phosphites and phenyl azide. The free triazenes are easily isolated from the solutions of the salts by acidification with hydrochloric acid.

The dialkylphosphoryl-N-phenyltriazenes are evidently stronger acids than the dialkyl phosphites. This follows from the fact that the reaction of diethyl phosphite with phenyl azide does not take place in presence of catalytic amounts of alcoholates.

#### EXPERIMENTAL

Sodium salts of dialkylphosphoryl-N-phenyltriazenes (I) were prepared by dropwise addition of phenyl azide to the sodium dialkyl phosphite in ether. Heat was developed during the addition and the color of the solution became light brown. After 24 hours the ethereal solutions of the sodium salts were evaporated in vacuum in the case of dipropyl- or dibutylphosphoryltriazenes. In the case of diethyl- or diisopropylphosphoryltriazenes the addition of the phenyl azide to the Na salt of the dialkyl phosphite in ether led at first to formation of a homogeneous solution from which, after 1-2 hours, the sodium salt came down.

Example. The sodium salt of diethylphosphoryl-N-phenyltriazene was prepared from 13.8 g (0.1 mole) of diethyl phosphite, 2.3 g (0.1 mole) of sodium and 11.9 g (0.1 mole) phenyl azide in 30 ml ether. Crystals came down and were collected and washed with ether; yield 10.2 g (68.5%; m.p. 145-145.5°). The salt was purified by reprecipitation with ligroine (b.p. 37-62°) from dry chloroform. It is soluble in alcohol, dioxane, water (the solution has an alkaline reaction) and hot benzene, insoluble in ligroine.

The sodium salts of dipropyl- and diisopropylphosphoryl-triazenes were similarly purified. The sodium salt of dibutylphosphoryl-N-phenyltriazene was recrystallized from ligroine.

Preparation of free dialkylphosphoryl-N-phenyltriazenes (II). Method A. (via the triethylammonium salts of dialkyl phosphites). No visible changes occurred on addition of phenyl azide to a mixture of dialkyl phosphite and triethylamine. Only in the case of dimethyl phosphite does a violent reaction take place (5-10 minutes after mixing of the reactants). The phenyl azide was therefore added dropwise to the solution of dimethyl phosphite and triethylamine in ether. After 1-2 days' standing, the volatile products were removed in vacuum.

Dimethylphosphoryl-N-phenyltriazene was prepared from 2.2 g (0.02 mole) dimethyl phosphite, 2 g (0.02 mole) triethylamine in 5 ml absolute ether and 2.4 g (0.02 mole) phenyl azide. The crystalline precipitate, obtained after removal of the volatile products, was pressed on porous plate to give 1.4 g (30.4%) of colorless crystals in the form of needles. The compound was precipitated from chloroform with ligroine. During determination of the melting point, the capillary containing the specimen was immersed in sulfuric acid hexated to 90°.

Diethylphosphoryl-N-phenyltriazene was prepared from 4.1 g (0.03 mole) of diethyl phosphite, 3 g (0.03 mole) triethylamine and 3.6 g (0.03 mole) phenyl azide. The crystals were pressed on a porous plate (3 g, 50%); m. p. 81-83°. Two precipitations from chloroform with ligroine gave the pure substance; colorless,



pentagonal plates, soluble in ether, alcohol and aqueous potassium hydroxide solution, insoluble in water, aqueous potassium carbonate and ligroine.

Diisopropylphosphoryl-N-phenyltriazene was prepared from 3.3 g (0.02 mole) of diisopropyl phosphite, 2 g (0.02 mole) triethylamine and 2.4 g (0.02 mole) phenyl azide. The oily residue could be crystallized by partial evaporation of the solution in ligroine and could be purified by recrystallization from chloroform while evaporating on a paraffin wax bath.

**Method B.** Ethereal solutions of the sodium salts of dialkylphosphoryl-N-phenyltriazenes were evaporated in vacuum, the residue was dissolved in water, and impurities were extracted with benzene. The free phosphoryltriazenes were isolated by acidification with dilute hydrochloric acid until weakly acidic to congo.

Dibutylphosphoryl-N-phenyltriazene was obtained from 1.340 g of sodium salt of dibutylphosphoryl-N-phenyltriazene and 0.247 g glacial acetic acid (equimolar quantities) in 8 ml ether. The precipitated sodium acetate was separated after 4 hours; the ether and volatile impurities were removed in vacuum (towards the end at 2 mm and 40°). 1.128 g of viscous, light-brown liquid was obtained;  $n_D^{20}$  1.5220; soluble in organic solvents, insoluble in water.

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THE CATALYTIC SYNTHESIS OF p-NITRO-, AMINO-  
AND SULFAMIDO DERIVATIVES OF 2-PHENYLQUINOLINE AND  
2-PHENYL-5,6-BENZOQUINOLINE

N. S. Kozlov and O. K. Kozminykh

(Presented by Academician A.A. Balandin, March 1, 1957)

Single representatives of nitro and amino derivatives of 2-phenylquinoline and of 2-phenyl-5,6-benzoquinoline have been described in the literature [1-3], and sulfamido derivatives of this series are not mentioned in the literature. Nevertheless, some amines [4] and sulfamides [4,5] of the quinoline series are known to possess strong antibacterial activity.

We prepared nitro derivatives of 2-phenylquinoline by the known method [6-9] of joint catalytic condensation of acetylene with aromatic amines and aromatic aldehydes. Compounds I-III (Table 1) were synthesized by this route. We condensed p-nitrobenzaldehyde and the following aromatic amines: p-anisidine, p-phenetidine and 2-naphthylamine. We converted the nitro compounds into amines by the usual reduction methods and so obtained compounds IV-VI (Table 1). From the amines were synthesized a series of sulfamido derivatives of 2-phenylquinoline and 2-phenyl-5,6-benzoquinoline (compounds VII-XXX in Table 2) by condensation of the amines in a pyridine medium with the acid chlorides of various sulfonic acids: benzene sulfochloride, 8-pyridine sulfochloride, p-methoxybenzene sulfochloride, m-nitrobenzene sulfochloride, m- and p-acetylaminobenzene sulfochlorides.

None of the compounds listed (I-XXX, Table 1 and 2) has been described in the literature.

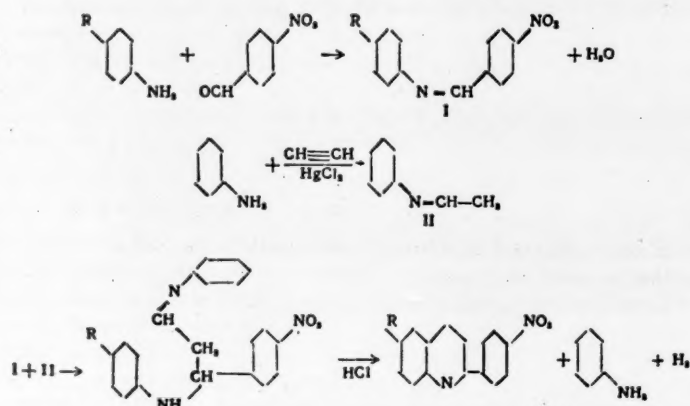
In the present work we effected considerable improvements in the method of synthesis of 2-phenyl derivatives of quinoline previously proposed by N. S. Kozlov [10,11], starting from acetylene, aromatic amines and aldehydes. A mixture of primary aromatic amine (2 moles) and aromatic aldehyde (1 mole) is saturated with acetylene in presence of a catalyst. According to our theory of the mechanism of the reaction, one half of the aromatic amine (1 mole) reacts with the aromatic aldehyde to form a Schiff base; the other half of the amine reacts with the acetylene to form the corresponding monoethylidene base. The two bases then react with one another to give an intermediate product which in one case was isolated; its structure was established [12]. The reaction mass in which the intermediate product is formed is then cyclized by the thermal method or by heating with 10% hydrochloric acid, and the intermediate product is converted into a 2-phenyl derivative of the quinoline series.

During the operation of such syntheses we observed that not all aromatic amines react with equal facility with acetylene; the most active amine was found to be aniline. The monoethylideneaniline base formed by aniline and acetylene reacts the most energetically with any of the Schiff bases and the resultant intermediate product possesses a great tendency to cyclize to the quinoline base. On the basis of these observations we developed a new method of synthesis of phenylquinoline bases, as follows: having obtained a Schiff base from a given aromatic aldehyde and aromatic amine, we added to it an equimolar amount of aniline and saturated the resultant reaction mass with acetylene in presence of a catalyst. Replacement of one half of the amount of aromatic amine by aniline greatly facilitates the synthesis of phenylquinoline bases, increases the yield of product and confirms the earlier concepts of N. S. Kozlov [13,14] about the mechanism of these syntheses. The syntheses of nitro derivatives of 2-phenylquinoline and 5,6-benzoquinoline can accordingly now be represented by the following mechanism:

TABLE 1

Compound No.	Compound and its empirical formula	M.p. deg C	Calculated(%)			Found (%)			M.p. of picrate	Pt of platinate, %	
			C	H	N	C	H	N		Calc.	Found
I	6-methoxy-2-(4'-nitrophenyl)quinoline $C_{16}H_{13}O_3N_2$	156-157	68.56	4.81	9.00	68.54	4.54	9.03	222-224 (decomp.)	20.11	19.91
II	6-ethoxy-2-(4'-nitrophenyl)quinoline $C_{18}H_{15}O_3N_2$	140-141	69.37	4.79	9.51	68.67	4.41	10.12	187-188 (decomp.)	19.65	19.57
III	2-(4'-nitrophenyl)-5,6-benzobenzquinoline $C_{21}H_{15}O_3N_2$	196.5-197	75.98	4.02	9.32	69.11	4.01	9.33	142-143	19.31	19.50
IV	6-methoxy-2-(4'-aminophenyl)quinoline $C_{16}H_{13}ON_2$	220-221	76.77	5.63	11.10	76.02	4.22	9.41	189-190 (decomp.)	21.44	21.42
V	6-ethoxy-2-(4'-aminophenyl)quinoline $C_{18}H_{15}ON_2$	188-189	77.24	6.10	10.50	76.99	5.85	11.11	203-205 (decomp.)	20.79	21.23
VI	2-(4'-aminophenyl)-5,6-benzobenzquinoline $C_{21}H_{15}N_2$	218-219	84.41	5.22	10.36	77.48	6.32	10.38	181-182	20.53	20.60
						84.51	5.29	10.37			20.38
						84.59	5.49	10.26			20.24





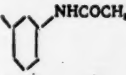
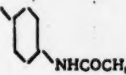


Note: Melting points of acetyl derivatives: IV) 234-235°; V) 229°; VI) 250-251°.



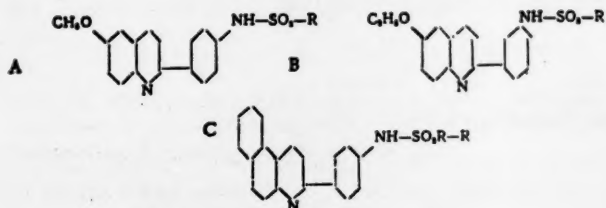
## EXPERIMENTAL

Nitro derivatives of 2-phenylquinoline were prepared by the following procedure. A crystalline Schiff base was first prepared by heating an equimolar mixture of aromatic amine and p-nitrobenzaldehyde in alcoholic solutions. To the Schiff base dissolved in toluene) was added an equimolar amount of aniline and catalyst (mercuric chloride in amount equal to 10% of the total mass), and the mixture was saturated with acetylene for 15-20 hours while heating to 80-90° on a water bath. After completion of saturation, a 1:2 mixture of conc. hydrochloric acid and alcohol was added to the mass which was then heated for 30 minutes on a water bath. The toluene layer was poured off, and the alcoholic solution (after cooling) deposited a crystalline precipitate of the hydrochloride of the product which was collected, purified by crystallization and dissolved in pyridine. The pyridine converted the salt to the base which was then crystallized from

TABLE 2

R	A				B				C			
	Compound number	M.p. deg C	N <sub>calcd.</sub> %	N <sub>found</sub> %	Compound number	M.p. deg C	N <sub>calcd.</sub> %	N <sub>found</sub> %	Compound number	M.p. deg C	N <sub>calcd.</sub> %	N <sub>found</sub> %
	VII	222-223	7.17	7.33 7.44	VIII	206-207	6.92	7.05 6.91	IX	229-230	6.82	6.87 6.69
	X	224-225	10.73	10.63 10.67	XI	215- 215.5	10.36	10.28 10.41	XII	241 (decomp.)	10.21	10.14 10.03
	XIII	182-183	6.66	6.45 6.37	XIV	232-233	6.44	6.38 6.23	XV	229-230	6.36	6.47 6.54
	XVI	179-180	9.65	9.50 9.76	XVII	206-207	9.34	9.37 8.53	XVIII	228-229	9.22	9.11 9.27
	XIX	213-214	9.39	9.43 9.48	XX	209-211	9.10	8.79 8.92	XXI	250 (decomp.)	8.98	9.20 9.15
	XXII	243-244	9.39	9.28 9.10	XXIII	227-228	9.10	9.33 9.37	XXIV	216-216	8.98	8.79 8.90
	XXV	225-226	10.36	10.51 10.31	XXVI	241-242	10.17	9.91 10.00	XXVII	254-255	9.87	10.08 10.06
	XXVIII	255-257 (decomp.)	10.36	10.28 10.10	XXIX	226-227	10.17	10.37 10.39	XXX	225-227	9.87	9.60 9.85

Note: For VIII, XI, XV and XVI  $S_{\text{calc.}}$  (respectively) : 7.92; 7.90; 7.27 and 7.36%;  
 $S_{\text{found}}$  7.78; 7.98; 7.54 and 7.57%.



acetone or pyridine. The yield of nitro base was not less than 50-60%. Reduction of the nitro derivatives to amino derivatives of 2-phenylquinoline was effected with tin in conc. hydrochloric acid with addition of a small quantity of alcohol to the gradually thickening mixture. Reduction took place in 10-15 hours while heating on a water bath. The mass was then neutralized with a conc. solution of sodium hydroxide, the precipitate was separated and dried, and the product extracted with acetone in a Soxhlet apparatus. The product was purified by crystallization from acetone or pyridine.

Sulfamides were prepared by the literature procedure [15, 16]; similarly the acid chlorides of sulfonic acids [16-20].

We converted the prepared nitrosulfamides (XVI-XVIII) into amino derivatives by reduction with iron in glacial acetic acid to give compounds identical with compounds XXV-XXVII; the latter were also prepared by hydrolysis of the acetylaminosulfamides (XIX-XXI). In this manner the proposed structure of the sulfamides was confirmed.

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## THE OXIDATIVE BREAKDOWN OF CELLULOSE ETHERS

O.P. Kozmina, V.I. Kurlyankina and E.N. Matveeva

(Communicated by Academician V.A. Kargin, November 28, 1956)

Cellulose ethers in the form of films, coatings and other articles lose their elasticity and mechanical strength on exposure to the air and to heat. These changes are bound up with the action of oxygen [1-4]. In this paper we present some results of investigations of the oxidation of cellulose ethers by molecular oxygen.

Cellulose ethers and the cellulose from which they were prepared were heated (not above 200°) in a vessel with a porous bottom in a stream of air, oxygen and inert gas. To facilitate determination of the oxygen uptake, the ethers were oxidized in a closed system with internal circulation of the gases through an absorber (for elimination of volatile reaction products from the oxygen).

These experiments confirm that oxidation by oxygen is at the root of the thermal breakdown of cellulose ethers (Fig. 1).

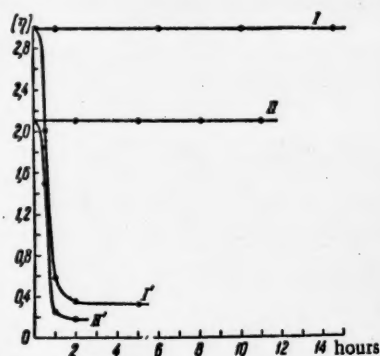


Fig. 1. Thermooxidative breakdown of cellulose ethers: I and I': characteristic viscosity of acetylcellulose at 200° (I in nitrogen, I' in oxygen); II and II': the same at 140° (II in nitrogen, II' in oxygen).

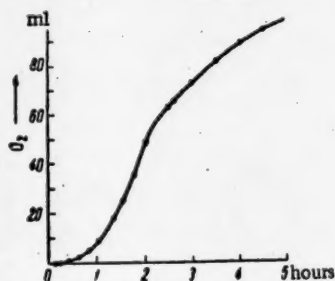


Fig. 2. Rate of oxygen uptake on oxidation of ethylcellulose at 130° (1.5 g of ethylcellulose).

The velocity and degree of destruction can be evaluated both from the change in viscosity of the solution of cellulose ethers and from the amount of absorbed oxygen and volatile products of oxidation. Absorption of oxygen is usually characterized by an integral type of curves (Fig. 2).

Induction periods characterize the oxidation of cellulose ethers by oxygen, and their duration depends upon the temperature and the length of time for which the ether had previously been stored. Oxidation of cellulose ethers is accompanied by lowering of their degree of polymerization, the loss of ethers groups and development of carbonyl or carboxyl group in the molecule of ether.



Aging and thermooxidative breakdown of ethylcellulose. A commercial ethylcellulose which had been purified and reprecipitated (under constant conditions) was examined; its ash content was about 0.01%.

Ethylcellulose is slowly oxidized by oxygen even at room temperature, peroxy groups being formed in the molecule and acetaldehyde being released.

If the peroxide groups in specimens of ethylcellulose which have been stored for a long time are destroyed, then oxidation induction periods (absent in the case of specimens stored for a long time) are again developed (Fig. 3).

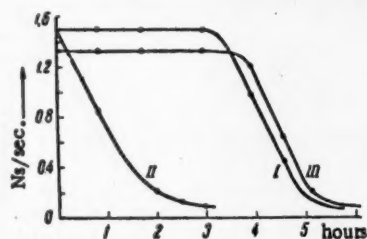


Fig. 3. Influence of peroxide groups in ethylcellulose on the speed of its thermooxidative breakdown (at 130°): I - specific viscosity one month after preparation of the sample; II - ditto after two years; III - ditto after removal (decomposition) of peroxide groups.

The thermooxidative breakdown of ethylcellulose reaches a high velocity at 125-140° and is accompanied by formation of liquid and gaseous products: acetaldehyde (main product), ethyl formate, ethyl alcohol, formic acid and carbon dioxide; oxidation of samples containing up to 0.5% ash in addition gives a small amount of methylglyoxal. All these products were isolated by fractional distillation in a vacuum column and were characterized.

The amount of acetaldehyde and ethoxyl groups in the ethyl alcohol and ethyl formate formed during the reaction corresponds to the fall in the percent of ethoxyl.

The characteristics of the ethylcellulose before and after oxidation are given in Table 1.

TABLE 1

Ethylcellulose	2 Yield, %	M.p. deg C	$[\eta]$	Mol. wt. $1 \cdot 10^3$	Elementary comp., %			Ethoxyl, %	Carboxyl %		Aldehyde groups %	Carbonic ester groups %
					C	H	O		total	uronic		
Original	—	185	1.65	45	56.77	9.09	34.14	47.1	0.11	0.05	none	none
Oxidized	93	125	0.11	—	54.47	8.36	37.16	36.9	—	—	—	—
a. Water-insoluble fraction (after dialysis)	—	—	—	—	—	—	—	—	—	—	—	—
b. Water-soluble fraction	64	134	0.12	2	—	—	—	38.0	1.35	1.0	2.7	0.2
	27	83	—	—	—	—	—	31.7	6.6	2.4	6.5	0.3

Note: The total content of carboxyls was determined by potentiometric titration in alcoholic solution; that of the aldehydic groups by determination of the iodine numbers; the molecular weight was estimated by sedimentation in the ultracentrifuge;  $[\eta]$  is the characteristic viscosity in acetone solution.

Spectral analysis likewise revealed an increase in the amount of carbonyl and hydroxyl groups in the oxidized ethylcellulose.

Methyl-, benzyl- and allylcellulose (and other ethers) are similarly oxidized and degraded by oxygen with loss of ether groups and release of formaldehyde, benzaldehyde and acrolein respectively as the main reaction products.

Oxidation of cellulose esters. Cellulose esters are degraded at higher temperatures. In the oxidation of acetylcellulose, one acetyl group per glucose chain is relatively easily split off in the form of acetic acid and acetaldehyde.



Oxidation takes a different course with cellulose esters of higher fatty acids — propionates and acetobutyrate (containing 40% butyric and 18% acetic). Propionates lose predominantly acetaldehyde and propionic acid as well as acetic acid; acetobutyrate give a mixture of propionic, butyric and acetic acids (ratio of 6:2:1) and of the corresponding aldehydes. The acids and aldehydes were separated from one another by fractional distillation and by chromatographic adsorption, while the individual aldehydes were isolated through their 2,4-dinitrophenylhydrazones.

In all cases carbon monoxide and dioxide were released in 1:2 ratio during oxidation of the esters.

Cellulose ethers are oxidized in a similar manner when irradiated with ultraviolet light.

The oxidation process was also studied on ethers of glucose and cellobiose which, like cellulose ethers, break down at the ether groups with loss of the corresponding volatile products.

Oxidation of ethers of cellulose and sugars is inhibited by antioxidants.

#### SUMMARY

1. Aging and thermooxidative breakdown of cellulose ethers and esters are caused by oxidation by atmospheric oxygen which proceeds through the stage of formation and breakdown of peroxides.

2. During oxidation the alkoxyl groups of ethers are split off in the form of the corresponding aldehydes and alcohols, while ester groups are split off in the form of the acids entering into the composition of the esters as well as in the form of acids and aldehydes with one carbon atom less than in the acidic group of the ester.

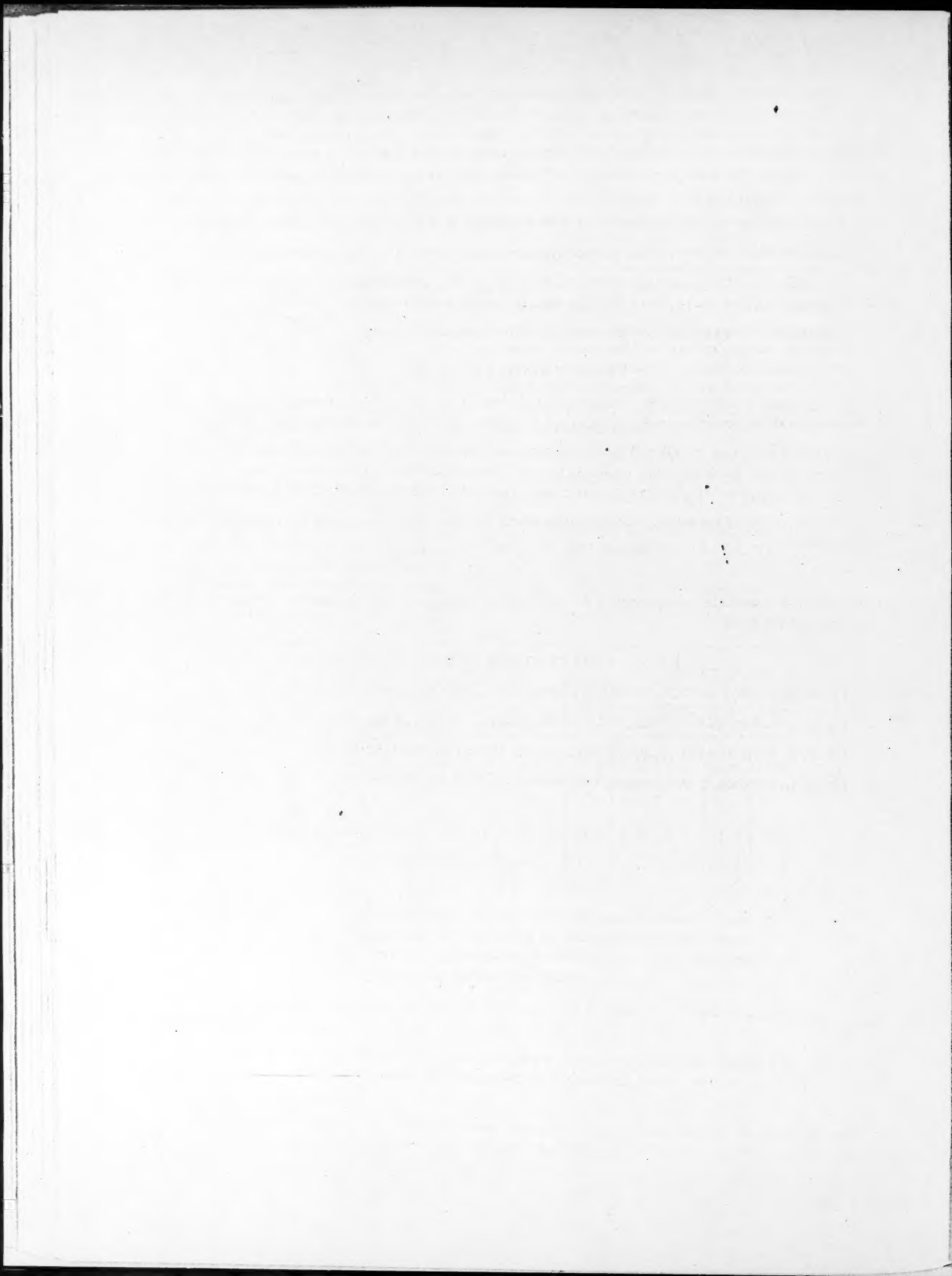
The molecules of the ethers become enriched with carboxyl and carbonyl groups in proportion to the loss of ether groups.

Institute of High-molecular Compounds of the Academy of  
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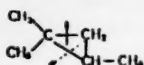
# CATALYTIC TRANSFORMATIONS OF 1,1,2-TRIMETHYLCYCLO- PROPANE IN PRESENCE OF PALLADIZED CARBON AND ACTIVATED CARBON

M. Yu. Lukina, S. V. Zotova and Academician B.A. Kazansky

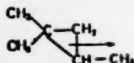
It has frequently been observed that cyclopropane and its homologs are capable of isomerizing to olefins in presence of certain catalysts (alumina [1-3], silica gel [4,5] and platinum black [6,1]). It should be appreciated that not in all these cases were the hydrocarbons obtained by isomerization identified with adequate certainty. Conflicting data have also appeared about the experimental conditions.

In the course of a study of the hydrogenolysis of hydrocarbons of the cyclopropane series [7-9] in presence of palladized and platinized carbon, we decided to establish whether or not these catalysts promote isomerization of a three-membered ring. The compound here investigated is 1,1,2-trimethylcyclopropane; the reaction was performed in a flow system in absence of hydrogen (in a nitrogen stream) at a temperature of 220° and at a space velocity of the hydrocarbon of 0.2 hour<sup>-1</sup>.

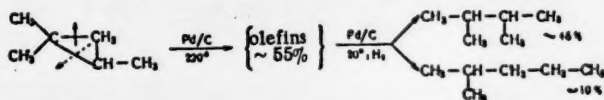
It was found that palladized carbon under these conditions isomerizes 1,1,2-trimethylcyclopropane to a mixture of olefins. Isomerization goes to the approximate extent of 55% with rupture mainly of the bond between the most and the least hydrogenated carbon atoms of the ring, while the other bond (adjoining the quaternary carbon atom) is ruptured to a lesser degree.



The bond between the most hydrogenated carbon atoms is the one that is ruptured during hydrogenolysis; it remains intact during isomerization.

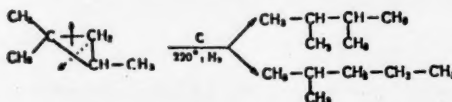


For more conclusive determination of the direction of rupture of the three-membered ring during isomerization, we hydrogenated the olefins formed and fractionated the product of hydrogenation in a high-efficiency column. The reaction may be represented by the following scheme:

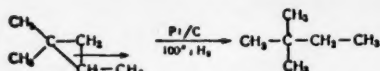


According to the data in our possession, platinized carbon behaves like palladized carbon in this reaction; experimental material relating to this catalyst will be published later.

We also studied the behavior of 1,1,2-trimethylcyclopropane in a nitrogen stream at the same temperature and space velocity in presence of activated carbon (a support used for the preparation of platinum and palladium catalysts). Carbon was found to be an even more active isomerization catalyst than platinum and palladium catalysts. Thus, in presence of carbon, 1,1,2-trimethylcyclopropane is completely converted into a mixture of olefins, the hydrogenation of which (followed by distillation) gave approx. 80% 2,3-dimethylbutane and approx. 20% 2-methylpentane. We likewise investigated the behavior of 1,1,2-trimethylcyclopropane when passed under the same conditions over activated carbon but in a hydrogen stream instead of a nitrogen stream. It was found that, apart from isomerization of 1,1,2-trimethylcyclopropane, the mixture of olefins formed then underwent hydrogenation. It should be noted that the carbon was not the active hydrogenation catalyst and was appreciably poisoned with progressive passage of the hydrocarbon. Only on passing small portions of hydrocarbon from the start was a saturated catalyzate obtained. Preparation of 25 ml of saturated catalyzate necessitated three successive passes through a fresh portion of activated carbon. Fractional distillation of the catalyzate showed that a mixture of 2,3-dimethylbutane and 2-methylpentane was then formed. The process can therefore be represented thus:



Comparison of this reaction with the hydrogenolysis of 1,1,2-trimethylcyclopropane [7] in presence of platinized carbon



enables us to draw the following conclusions:

1. Two processes can take place during the catalyzed addition of hydrogen to alkylcyclopropanes: hydrogenolysis of the three-membered ring with ring fission, and isomerization to olefins followed by their hydrogenation.
2. Hydrogenolysis of the alkylcyclopropanes does not go through their intermediate isomerization to olefins; otherwise the end-products of both reactions would have been identical.
3. Activated carbon can catalyze not only the isomerization of alkylcyclopropanes but also the hydrogenation of the resultant olefinic hydrocarbons.

#### EXPERIMENTAL

Isomerization of 1,1,2-trimethylcyclopropane in presence of palladized carbon. 50 ml of 20% palladized carbon, prepared by Zelinsky's procedure [10], was placed in a catalytic tube. The catalyst was reduced in a hydrogen stream at 300°, after which the temperature was lowered to the desired level, the hydrogen feed was interrupted, and hydrogen adsorbed by the catalyst was displaced from its surface with a definite amount of 1,1,2-trimethylcyclopropane which was thereby hydrogenated (this portion was rejected). 1,1,2-Trimethylcyclopropane was then passed over the catalyst at a space velocity of 0.2 hour<sup>-1</sup> in a weak current of nitrogen. The catalyzate had  $n_D^{20}$  1.3940 and rapidly decolorized bromine water. After hydrogenation in a hydrogenation flask at room temperature in presence of palladized carbon, 78 g of the mixture was fractionated in a 100-plate column. Results of the fractionation are set forth in Table 1 and plotted in Fig. 1 (curve a); the constants of the original 1,1,2-trimethylcyclopropane and of the hydrocarbons that may be present in the mixture are given in Table 2.

TABLE 1

Fraction	A-mount in g	B.p. deg C	$n_D^{20}$	$d_4^{20}$
I	8.9	48.6-52.0	1.3800	0.6780
II	20.4	52.0-52.8	1.3860	0.6944
III	10.9	52.8-57.6	1.3810	
IV	25.4	57.6-57.7	1.3750	0.6612
V	4.6	57.7-59.8	1.3730	0.6565
VI	1.4	59.8-61.0	1.3717	0.6537*
VII	5.3	61.0-86.4	1.3730	0.6548

\* 20 ml of n-octane was added to the distillation flask as a displacing agent.

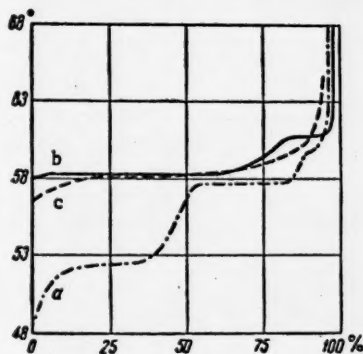


Fig. 1

water gave a negative reaction with diphenylamine, and dried.

Ash content of the carbon 0.2%. Activity (ether value) 24%.

The isomerization of 1,1,2-trimethylcyclopropane was carried out in exactly the same manner as described above;  $n_D^{20}$  of isomerizate 1.4035. The product of isomerization was hydrogenated in a flask in presence of palladized carbon; 28.2 g of the resultant mixture of hydrocarbons was fractionated in a 100-plate column. Results of the fractionation are set forth in Table 3 and plotted in Fig. 1 (curve b).

TABLE 3

Fraction	A-mount in g	B.p. in deg C (at 760 mm)	$n_D^{20}$	$d_4^{20}$
I	1.3	58.0-58.2	1.3751	0.6624
II	16.5	58.2	1.3750	0.6616
III	6.5	58.2-60.7	1.3746	0.6595*
IV	2.9	60.7	1.3725	0.6556
V	1.0	60.7-81.8	1.3721	0.6550

\* 20 ml of n-octane was added to the distillation flask as displacing agent.

TABLE 2

Hydrocarbon	B.p. deg C (760 mm)	$n_D^{20}$	$d_4^{20}$
1,1,2-Trimethyl cyclopropane	52.5	1.3862	0.6947
2,2-Dimethylbutane [11]	49.741	1.36876	0.64915
2,3-Dimethylbutane [11]	57.988	1.37495	0.66164
2-Methylpentane [11]	60.271	1.37145	0.65316

On comparing the data of Tables 1 and 2, we can infer that fraction IV is 2,3-dimethylbutane, fraction VI (and in part fraction VII) is 2-methylpentane. Fraction II is unreacted 1,1,2-trimethylcyclopropane, and fractions III and V are intermediate fractions. Fraction I contains 1,1,2-trimethylcyclopropane and a trace of 2,2-dimethylbutane, which could have been formed by hydrogenolysis of 1,1,2-trimethylcyclopropane dissolved in the palladized carbon.

Consequently, judging by the fractional distillation data, isomerization went to the extent of approximately 55%, 45% being 2,3-dimethylbutane and about 10% 2-methylpentane.

Isomerization of 1,1,2-trimethylcyclopropane in presence of activated carbon. The activated carbon was first subjected to our standard treatment as applied to platinized and palladized carbon. The material was heated with caustic alkali solution, thoroughly washed with water until neutral, heated with dilute nitric acid, thoroughly washed with distilled water until the wash

A comparison of the data of Table 3 with the constants given in Table 2 shows that fraction II is 2,3-dimethylbutane, fraction IV is mainly 2-methylpentane, and fraction III is intermediate.

The fractionation data thus indicate that isomerization in presence of activated carbon went to completion. The hydrogenated isomerizate is a mixture of approx. 80% 2,3-dimethylbutane and approx. 20% 2-methylpentane.

TABLE 4

Experiment No.	Amount (in ml) of 1,1,2-trimethylcyclopropane taken	B.p. in deg C (at 760 mm)			
		$n_D^{20}$	$d_4^{20}$	aniline point	reaction with bromine water
1	2	1.3748	0.6606	71.4	not decolorized
2	3	1.3745	0.6602	—	•
3	6	1.3750	0.6612	69.8	•
4	30	1.3750*	—	—	•

\* The constants given are those of a catalyzate obtained by three passes over activated carbon.

TABLE 5

Fraction	Amount in ml	B.p. in deg C (at 760 mm)	$n_D^{20}$	$d_4^{20}$
1	5.0	56.5—57.9	1.3750	0.6616
2	7.5	57.9—58.1	1.3749	0.6612
3	3.5	58.1—58.5	1.3745	0.6610
4	3.0	58.6—59.1	1.3739	0.6589
5	3.0	59.1—60.3	1.3735	0.6571

Hydrogenation of 1,1,2-trimethylcyclopropane in presence of activated carbon. Experiments were run at a temperature of 220° and a space velocity of 0.2 hour<sup>-1</sup>, as described above except that the 1,1,2-trimethylcyclopropane was passed over the activated carbon in a hydrogen stream. Results are given in Table 4. 28 g of combined catalyzates was fractionated in a 50-plate column. Results of the fractionation are set forth in Table 5 and plotted in Fig. 1 (curve c).

Comparison between the data of Tables 2 and 5 shows that fractions 1,2 and 3 are mainly 2,3-dimethylbutane and that fractions 4 and 5 contain a mixture of 2,3-dimethylbutane and 2-methylpentane.

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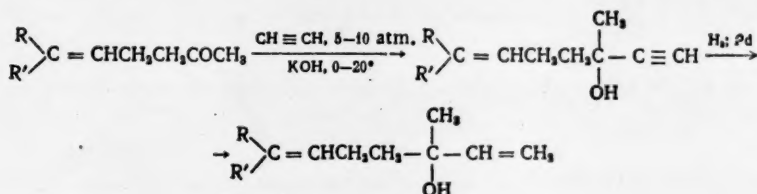
\* In Russian.



THE CONDENSATION OF ACETYLENE WITH METHYLHEPTENONE  
AND ITS ANALOGS  
SYNTHESIS OF LINALOOL AND ITS ANALOGS

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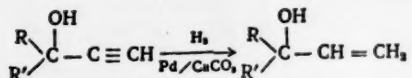
Some years ago in our laboratory we developed a simple method of synthesis of diverse acetylenic alcohols by condensation of aldehydes and ketones with acetylene in presence of pulverized potassium hydroxide under slight pressure (5-10 atm.) [1]. It was of interest to apply this method to the condensation of acetylene with methylheptenone and similar ketones [2] in order to obtain the corresponding acetylenic alcohols which, by partial hydrogenation with Pd catalyst, could easily be converted into linalool and its analogs:



Up to now such condensations have usually been realized in presence of metallic sodium in solution in liquid ammonia, and the yield of dehydrolinalool so obtained has amounted to about 80% [3].

It was found that methylheptenone and its diverse analogs, in presence of pulverized potassium hydroxide, condense with remarkable facility with acetylene under a pressure of 5-10 atm. at a temperature of 0-20° to give the corresponding tertiary acetylenic alcohols in nearly quantitative yield (over 90%). This condensation can also be effected without application of pressure, but the reaction is then many times slower and gives lower yields of alcohols (60-80%).

In our laboratory it was previously shown [4] that acetylenic alcohols containing an unsubstituted acetylenic hydrogen are hydrogenated in presence of palladium on calcium carbonate or coppered zinc dust with strict selectivity to form the corresponding vinyl alcohols in nearly theoretical yield:



With other catalysts (Ni, Pt) acetylenic alcohols are hydrogenated nonselectively and such catalysts are therefore unsuitable for the preparation of pure vinyl alcohols.

A similar picture is observed in the hydrogenation of the above-described acetylenic alcohols, obtained by condensation of acetylene with methylheptenone and its analogs. In presence of Pd catalyst these acetylenic alcohols likewise undergo strictly selective hydrogenation with formation of linalool and its analogs in nearly theoretical yield. The purity of the vinyl alcohols (linalool and its analogs) was checked with the help of the acetylene test (with an ammoniacal solution of copper oxide or silver oxide), the sensitivity of which was determined in special experiments and found to be 0.2-0.3%. On hydrogenation of acetylenic alcohols over Pd catalyst, the test for acetylene always becomes negative at the theoretical point, i.e. when exactly one molecule of hydrogen has combined. The acetylenic alcohols obtained in the present work are listed in Table 1.

TABLE 1

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{R} \diagup \text{C} = \text{CHCH}_2\text{CH}_2\text{C} - \text{C} \equiv \text{CH} \\ \text{R}' \diagdown \quad | \\ \quad \text{OH} \end{array}$$

Pre- para- tion No.	R	R'	B.p. deg C <sub>mm</sub>	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	MR		Analysis %. %				Yield, %
						found	calcd.	found		calcd.		
								C	H	C	H	
I	H	H	55-58/10	1.4530	0.8904	38.09	38.14	76.98	9.74	77.36	9.74	83
II	CH <sub>3</sub>	H	66-67/8	1.4570	0.8774	42.87	42.76	78.20	10.21	78.17	10.20	83
III	CH <sub>3</sub>	Cl	81-82/3	1.4800	1.0260	47.79	47.62	62.81	7.66	62.60	7.53	90
IV	CH <sub>3</sub>	CH <sub>3</sub>	81-82/10	1.4634	0.8788	47.63	47.44	78.90	10.45	78.94	10.52	82
V	CH <sub>3</sub>	CH <sub>3</sub>	81-83/2	1.4629	0.8826	51.87	51.99	79.52	11.17	79.52	10.84	91
VI	CH <sub>3</sub>	iso-C <sub>2</sub> H <sub>5</sub>	84-85/2	1.4642	0.8738	56.84	56.67	79.81	11.10	80.00	11.11	90
VII	CH <sub>3</sub>	tert.-C <sub>4</sub> H <sub>9</sub>	100-101/8	1.4680	0.8772	61.48	61.23	80.32	11.46	80.41	11.33	91
VIII	iso-C <sub>4</sub> H <sub>9</sub>	iso-C <sub>4</sub> H <sub>9</sub>	92/1.5	1.4610	0.8687	66.04	65.84	80.78	11.41	80.70	11.61	93
IX	(CH <sub>3</sub> ) <sub>2</sub>		89-91/1	1.4925	0.9409	59.25	59.09	81.30	10.44	81.25	10.41	87
X	3-me- thyldehy- drolinal.		104-106/13	1.4684	0.8886	52.01	51.99	79.53	11.12	79.45	10.90	88

\* Repeat analyses are omitted throughout.

Partial hydrogenation of the acetylenic alcohols listed above with Pd catalyst gave linalool and its analogs (Table 2).

TABLE 2

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{R} \diagup \text{C} = \text{CHCH}_2\text{CH}_2\text{C} - \text{CH} = \text{CH}_2 \\ \text{R}' \diagdown \quad | \\ \quad \text{OH} \end{array}$$

Pre- para- tion No.	R	R'	B.p.in deg C/mm	$n_D^{20}$	$d_4^{20}$	MR		Analysis, %				Yield %
						found	calcd.	found		calcd.		
								C	H	C	H	
XI	H	H	54-55/10	1.4500	0.8549	39.64	39.74	75.99	11.30	76.12	11.19	95
XII	CH <sub>3</sub>	H	58-60/8	1.4482	0.8488	44.28	44.35	77.33	11.50	77.07	11.51	97
XIII	CH <sub>3</sub>	Cl	65-66/3	1.4787	1.0060	49.03	49.22	61.69	8.63	61.89	8.59	93
XIV	CH <sub>3</sub>	CH <sub>3</sub>	80-81/10	1.4622	0.8664	48.95	48.97	77.64	11.86	77.80	11.68	96
XV	CH <sub>3</sub>	CH <sub>3</sub>	80-82/2	1.4622	0.8653	53.75	53.58	78.76	12.09	78.51	11.98	95
XVI	CH <sub>3</sub>	iso-C <sub>2</sub> H <sub>5</sub>	87-88/3	1.4632	0.8575	58.48	58.27	78.97	12.00	79.12	12.09	95
XVII	CH <sub>3</sub>	tert.-C <sub>4</sub> H <sub>9</sub>	103-104/9	1.4659	0.8632	62.88	62.82	79.85	12.20	79.64	12.24	96
XVIII	iso-C <sub>4</sub> H <sub>9</sub>	iso-C <sub>4</sub> H <sub>9</sub>	92/1.5	1.4610	0.8579	67.50	67.44	79.85	12.52	80.00	12.45	95
XIX	(CH <sub>3</sub> ) <sub>2</sub>		88-89/1	1.4918	0.9227	60.97	60.63	80.15	11.28	80.47	11.32	92
XX	3-me- thylli- nalool		86-88/7	1.4678	0.8746	53.43	53.59	78.40	12.00	78.57	11.98	91

## EXPERIMENTAL

All condensation of methylheptenone and its analogs with acetylene under pressure were performed in a steel reactor with a capacity of 2 or 6 liters [1]. Selective hydrogenation of the resultant acetylenic alcohols was carried out without a solvent in presence of small amounts of palladium on calcium carbonate in the steel reactor under a hydrogen pressure of 3-5 atm. (quantity of more than 200 g) or in an ordinary glass hydrogen flask (quantity less than 200 g).

**Dehydrolinalool (IV).** Into a 6-liter steel reactor were charged 3500 ml dry ether, 360 g pulverized potassium hydroxide and 20 ml ethyl alcohol. The mixture (vigorously stirred) was saturated with acetylene at 0° and a pressure of 6 atm, which was maintained throughout the experiment. 680 g of methylheptenone was fed into the reactor in the course of 1 1/2 hours, after which the stirring of the reaction mass was continued for another 3 hours. Towards the close of the experiment the temperature was slowly raised to 20°. The pressure of the acetylene was then let down and 720 ml water was added to the stirred mixture. The ether layer was separated and the aqueous layer extracted with ether. The combined ethereal extracts were neutralized with carbon dioxide gas and dried with magnesium sulfate. Distillation gave 759 g (92%) of dehydrolinalool (IV) with b.p. 81-82° mm;  $n_D^{20}$  1.4634;  $d_4^{20}$  0.8788.

**Linalool (XIV).** 740 g of dehydrolinalool was hydrogenated in presence of 1.2 g Pd/CaCO<sub>3</sub> catalyst (containing about 5% Pd) in a 2-liter autoclave at 20-35° and a hydrogen pressure of 1-3 atm. 110 liters hydrogen was absorbed (theoretical amount) in the course of 2 hours 20 min; the acetylene test became negative and hydrogenation was stopped; the catalyst was filtered off and the product distilled in vacuum to give 713 g (95%) linalool (XIV) with b.p. 81-82°/10 mm;  $n_D^{20}$  1.4622.

**3-Methyldehydrolinalool (X).** A mixture of 160 g pulverized potassium hydroxide, 2000 ml dry ether and 20 ml ethanol was saturated with acetylene at 0° and a pressure of 7.5 atm.

204 g of 2,3-dimethyl-2-hepten-6-one was added in the course of 40 min. and stirring was then continued for a further 5 hours. The mass was worked up in the usual manner and fractionally distilled to give 206 g (88%) of 3-methyldehydrolinalool (X) with b.p. 104-106°/14 mm;  $n_D^{20}$  1.4687 [5].

**3-Methylinalool (XX).** 35 g of 3-methyldehydrolinalool was hydrogenated in a glass flask in presence of 0.1 g Pd/CaCO<sub>3</sub> catalyst. Hydrogenation was stopped after 5300 ml hydrogen had been taken up (19°, 730 mm). The catalyst was filtered off and the product fractionated. Yield 32.1 g (91%) of 3-methylinalool (XX) with b.p. 86-88°/7 mm;  $n_D^{20}$  1.4678 [5].

**2-Chloro-6-methyl-2-octen-7-yn-6-ol (III).** A mixture of 350 g pulverized potassium hydroxide, 2000 ml dry ether and 20 ml ethanol was saturate with acetylene at 8° and a pressure of 6 atm. In the course of 2 1/2 hours 355 g of 2-chloro-2-hepten-6-one was introduced into the reactor and stirring was continued for another 2 hours. Working up in the usual manner gave 377.5 g of 2-chloro-6-methyl-2-octen-7-yn-6-ol (III) with b.p. 81-82°/3 mm;  $n_D^{20}$  1.4809.

Hydrogenation of 100 g of this alcohol in presence of Pd/CaCO<sub>3</sub> catalyst resulted in absorption of 1450 ml of hydrogen (19°, 746 mm), after which the hydrogenation was stopped. The catalyst was filtered off and the product distilled in vacuum to give 93.6 g (93%) of 2-chloro-6-methyl-2,7-octadien-6-ol (XIII) with b.p. 65-66°/3 mm;  $n_D^{20}$  1.4787.

**2,2,3,7-Tetramethyl-3-nonen-8-yn-7-ol (VII).** 120 g pulverized potassium hydroxide, 1500 ml dry ether and 15 ml ethanol were saturated with acetylene at 10° and a pressure of 6.5 atm. In the course of 1 hour 90 g 2,2,3-trimethyl-3-octen-7-one was charged into the reactor and stirring continued for another 4 hours. The usual treatment led to isolation of 95 g (91%) of 2,2,3,7-tetramethyl-3-nonen-8-yn-7-ol (VII) with b.p. 100-101°/8 mm;  $n_D^{20}$  1.4680.

48.5 g of this alcohol (VII) was hydrogenated with hydrogen in presence of Pd/CaCO<sub>3</sub> catalyst. After absorption of 6300 ml hydrogen (20°, 728 mm), hydrogenation was interrupted. Yield 47.5 g (98%) of 2,2,3,7-tetramethyl-3,8-nonadien-7-ol (XVII) with b.p. 103-104°/9 mm;  $n_D^{20}$  1.4659.

**4-Methyl-1-cyclohexylden-5-hexyn-4-ol (IX).** 130 g of pulverized potassium hydroxide, 900 ml dry ether and 15 ml ethanol were saturated with acetylene at 0° and a pressure of 9 atm. 100 g of 1-cyclohexyldene-pentan-4-one was charged into the reactor in the course of 30 min. and stirring was continued for another 3 hours. Working up in the usual manner gave 100.3 g (87%) of 4-methyl-1-cyclohexylden-5-hexyl-4-ol (IX) with b.p. 89-91°/1 mm;  $n_D^{20}$  1.4925.

Selective hydrogenation of 23.1 g of the acetylenic alcohol (IX) in presence of Pd/CaCO<sub>3</sub> catalyst (hydrogenation was stopped when 3050 ml hydrogen at 19° and 725 mm had been taken up) gave 21.5 g (92%) of 4-methyl-1-cyclohexyliden-5-hexen-4-ol (XIX) with b.p. 88-89°/1 mm;  $n_D^{20}$  1.4918.

The other compounds listed in Table 1 and 2 were obtained in similar fashion.

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## SYNTHESIS OF ALKYLFERROCENES BY THE FRIEDEL-CRAFTS REACTION

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We were the first [1] to describe the alkylation of ferrocene with alkyl halides in presence of anhydrous aluminum chloride. Excess of the alkyl halide was used as the solvent.

In the present work we succeeded in carrying out the same reaction without using excess of alkyl halide and at the same time we increased the yield of mono- and dialkyl derivatives of ferrocene. *n*-Heptane or absolute ligroline (b.p. 60-80°) was used as solvent.

By direct alkylation of ferrocene with alkyl halides (methyl chloride, isopropyl chloride) or unsaturated hydrocarbons (ethylene) we obtained the previously unknown alkylferrocenes: methylferrocene, dimethylferrocenes, isopropylferrocene, diisopropylferrocenes, and isomeric diethylferrocenes both of whose alkyl groups were in the same cyclopentadiene ring.

The isomeric alkylferrocenes were fractionated by chromatography on anhydrous alumina, making use of an automatic flow refractometer of the PRA-25 system of L.V. Obrimov, V.I. Dianov - Klov and E. A. Shibakov [2].

Comparison of the infra-red spectra of the isomeric diethylferrocenes prepared by us (I and II) and the diethylferrocene III prepared by one of us and Volkenau [4] by reduction of diacetylferrocene gave the following results.

Diethylferrocene III, which contains ethyl groups in different cyclopentadienyl rings [4], does not possess characteristic frequencies in the 1000-1200  $\text{cm}^{-1}$  region. Diethylferrocenes I and II possess frequencies of 998 and 1107  $\text{cm}^{-1}$ , in addition to which compound II possesses another frequency at 1277  $\text{cm}^{-1}$  of great intensity (this is entirely absent from compounds I and III); consequently, I and II are isomers of III, i.e. they contain both of the ethyl groups in one cyclopentadiene ring. Methyl- and dimethylferrocenes and isopropyl and diisopropylferrocenes likewise have characteristic frequencies in the 1000 and 1107  $\text{cm}^{-1}$  regions (characteristic of ferrocene itself and its mono-substituted derivatives). \*

Consequently, the introduction of a first alkyl group into a cyclopentadiene nucleus facilitates the entry of a second alkyl into the same ring (a similar phenomenon is observed in the case of the aromatic nucleus); in this way a mixture of dialkylferrocenes with substituents in one ring is obtained.

### EXPERIMENTAL

**Methylferrocene.** A stream of gaseous methyl chloride was passed into a solution of 40 g ferrocene in 325 ml *n*-heptane; the methyl chloride was prepared by the previously described procedure [3] from 820 g anhydrous zinc chloride, 525 ml conc. HCl, and 105 ml methyl alcohol. With heating to 55-60°, 30 g of aluminum chloride was gradually introduced. Heating was continued for 5 hours. After decomposition by the usual method, 20.4 g of liquid reaction product was obtained and 10 g of unreacted ferrocene was recovered. Fractional distillation of the liquid product followed by recrystallization from absolute ethyl alcohol gave 1.5 g of methylferrocene. M.p. 118-119°.

\* Measurements of the infra-red spectra were made by L.A. Kozitsin and B.V. Lokshin to whom we express our gratitude.

Found %: C 65.77; 65.80; H 5.87; 5.91; Fe 28.30; 28.26  $C_{11}H_{12}Fe$ . Calculated %: C 65.95; H 6.15 Fe 27.95.

Methylferrocene forms yellow, fluffy plates which are nearly odorless; soluble in all the common organic solvents, insoluble in water. It is appreciably more soluble than ferrocene in alcohol. 3.2 g of a mixture of isomers of dimethylferrocene was obtained; b.p. 127-128°/13 mm,  $n_D^{20}$  1.6001,  $d_4^{20}$  1.2646.

Found %: C 67.33; 67.48; H 6.56; 6.51; Fe 25.95; 25.91  $C_{12}H_{14}Fe$ . Calculated %: C 67.32; H 6.55; Fe 26.13

Dimethylferrocene is a dark red liquid with a camphor odor, readily soluble in the common organic solvents, insoluble in water.

In addition, we obtained 4.3 g of a mixture of other liquid products of methylation of ferrocene, b.p. 130-150°/13 mm, which were not closely studied.

Isomers of dimethylferrocene. By the same procedure, starting from 40 g ferrocene dissolved in 300 ml ligroine, 20 ml ethyl bromide and 10 g aluminum chloride, operating at 50-60° for 5-6 hours, 8.8 g of liquid products of reaction was obtained; 22.6 g of ferrocene was recovered (the mean yield of products of alkylation, reckoned on the original ferrocene (17.4 g) and the diethylferrocene obtained is 39%). The amount of monoethylferrocene separated from the alkylation products was 4.2 g, i.e. 18.5% of theory.

Fractionation of the products of reaction was effected by successive chromatographic resolution of fractions boiling at 106-108°/5 mm 118-123°/15 mm and 125-140°/15 mm on anhydrous alumina by the method described above. The following were obtained:

Ethylferrocene  $n_D^{20}$  = 1.6010;  $d_4^{20}$  = 1.2628 [1,4].  $MR_{found}$  = 58.06.

Diethylferrocene I  $n_D^{20}$  = 1.5822;  $d_4^{20}$  = 1.2002.  $MR_{found}$  = 67.35.

Found %: C 69.16; 69.24; H 7.39; 7.21; Fe 22.94; 22.73

Diethylferrocene II  $n_D^{20}$  = 1.5850;  $d_4^{20}$  = 1.2041.  $MR_{found}$  = 67.35.

Found %: C 69.35; 69.37; 47.28; 7.25; Fe 22.85; 22.91  $C_{14}H_{18}Fe$ . Calculated %: C 69.51; H 7.40; Fe 23.09

Isopropylferrocene. The same procedure was employed, starting from 40 g ferrocene dissolved in 300 ml absolute ligroine, 20 ml isopropyl chloride and 7.5 g anhydrous aluminum chloride 7.33 g of liquid product was obtained and 26.7 g of unreacted ferrocene was recovered. The liquid products were fractionated by successive chromatographic resolution of fractions boiling at 106-107°/3 mm, 115-120°/3 mm and 120-140°/3 mm on anhydrous alumina (weight 50 g, height of bed 40 cm, solvent n-heptane) using the PRA-25 automatic flow refractometer [2]. 2.3 g of isopropylferrocene was obtained;  $n_D^{20}$  = 1.5897;  $d_4^{20}$  = 1.2230.  $MR_{found}$  = 62.92.

Found %: C 68.58; 68.49; H 7.09; 7.07; Fe 23.49; 24.37  $C_{12}H_{16}Fe$ . Calculated %: C 68.50; H 7.06; Fe 24.44

Isopropylferrocene is a dark red liquid with a characteristic camphor odor, readily soluble in the common organic solvents, insoluble in water.

3.3 g of diisopropylferrocene was similarly prepared;  $n_D^{20}$  = 1.5815;  $d_4^{20}$  = 1.2160.

Found %: C 70.80; 71.01; H 7.84; 7.76; Fe 21.29; 21.31  $C_{16}H_{22}Fe$ . Calculated %: C 71.15; H 8.16 Fe 20.56

Dark-red liquid with a characteristic camphor odor, readily soluble in the common organic solvents, insoluble in water.

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\* See C. B. translation.

\*\* In Russian.

# THE PROBLEM OF THE CHROMATOGRAPHIC SEPARATION OF AROMATIC HYDROCARBONS FROM THEIR MIXTURES WITH ORGANIC SULFUR COMPOUNDS

R.D. Obolentsev and B. V. Aivazov

(Presented by Academician B.A. Kazansky, December 25, 1956)

Numerous attempts to isolate aromatic hydrocarbons free of organic sulphur compounds from sulfur-containing petroleum and their derived products with the help of adsorbents like silica gel and alumina gel have not been successful [1-3]. A report of some results of our own investigations may consequently be of interest.

With the objective of establishing the conditions of chromatographic separation of aromatic hydrocarbons from their mixture with organic sulfur compounds which are present in ligroine-kerosene distillates (i. e. relatively high-boiling petroleum fractions), we tested a series of adsorbents available from Russian sources — silica gel, alumina and activated carbon. Tests were made with artificial mixtures. We selected the method of frontal chromatography for evaluation of the adsorptive power of our adsorbents. Adsorption was effected from solutions of the tested substances in commercial isooctane in glass columns 50 cm high and 1 cm in diameter; the specific adsorptive power was determined from the volume retained (Table 1).

Inspection of Table 1 shows that the materials tested were typical polar adsorbents (silica gels), nonpolar adsorbents (carbons) and substances occupying an intermediate position (alumina). The values of specific adsorption presented in the table fluctuate over a wide range and depend on the nature both of the adsorbents and of the adsorbates; in a number of cases the specific adsorption of the aromatic hydrocarbons differs considerably from that of the organic sulfur compounds.

TABLE 1  
Specific Adsorption of Some Aromatic Hydrocarbons and Organic Sulfur Compounds from Their Solutions in Commercial Isooctane (in mm<sup>3</sup>/g)\*

Adsorbents	Substances adsorbed							
	aromatic hydrocarbons				sulfur-containing compounds			
	n-butylbenzene (a)*	naphthalene (b)	α-methyl-naphthalene (c)	di-n-butyl sulfide (A)	di-n-nonyl sulfide (B)	n-propyl-phenyl sulfide (C)	di-n-butyl disulfide (D)	benzylmercaptan (E)
Silicagels:								
ShSM	0.21	0.49	0.49	0.35	0.10	0.49	0.29	0.99
MSM	—	0.44	0.64	0.56	—	—	0.50	0.98
ASM	0.66	0.24	0.86	0.50	0.52	1.08	0.63	1.46
Alumina for chromatography	0.09	0.69	0.18	0.08	0.03	0.05	0.14	0.20
AR	0.44	0.46	0.35	0.18	0.06	0.44	0.20	0.88
BAU	—	0.74	1.23	1.67	0.44	1.38	1.02	1.54

\* In all cases the initial concentration of the solutions was 300 mm<sup>3</sup>/ liter.

\*\* a-c and A-E correspond to the letters in Fig. 1.

As an example we shall consider the chromatographic resolution of a complex mixture comprising aromatic hydrocarbons and organic sulfur compounds, the adsorption isotherms of which do not intersect; also there is no reciprocal influence of the components of the mixture. For the case in question the values of specific adsorption given in Table 1 clearly characterize the order of discharge of the components of the chromatogrammed mixture and give an indication of the possible completeness of resolution. By using different adsorbents and effecting successive and numerous chromatogrammings, it is possible to achieve complete resolution of the mixture subjected to chromatographic treatment. One variant of the possible schemes of such a series of chromatographic operations is shown in Fig. 1.

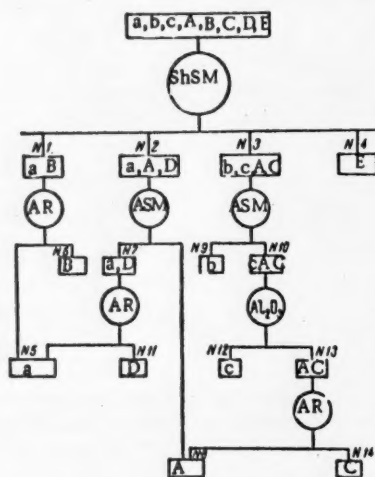


Fig. 1. A possible scheme of chromatographic resolution of a mixture of aromatic hydrocarbons and organic sulfur compounds: a - n-butylbenzene; b - naphthalene; c - methyl-naphthalene; A - di-n-butyl sulfide; B - di-n-nonyl sulfide; C - n-propylphenyl sulfide; D - di-n-butyl-disulfide; E - benzylmercaptan; ShSM - silica gel, ShSM brand; ASM - silica gel, ASM brand; AR - carbon, AR brand;  $Al_2O_3$  - alumina "for chromatography"; 1-14 - numbers of filtrates.

the process of checking of the chromatographic filtrates. Only n-butylbenzene, benzylmercaptan, di-n-butyl sulfide and di-n-nonyl sulfide were isolated in the pure state;  $\alpha$ -methyl-naphthalene, naphthalene, isohexylphenyl sulfide and di-n-dibutyl sulfide were not isolated in the pure state, as was assumed by the scheme given in Fig. 1. The lack of accord between the scheme and the final experimental results may be attributed to intersection of the adsorption isotherms and possibly also to the reciprocal influence of the components. We must assume that successful resolution of a mixture of aromatic hydrocarbons and organic sulfur compounds will require investigations of the adsorption isotherms of the largest possible number of the compounds in question.

We effected the separation of n-butylbenzene from its mixture with di-n-butyl sulfide, di-n-butyl disulfide and benzylmercaptan by chromatogramming under similar conditions on ASM silica gel. Displacement was effected with a solution of acetone in commercial isooctane (1:15 by volume).

\* Special experiments established that the values of specific adsorption of isohexylphenyl sulfide and n-propylphenyl sulfide on the tested adsorbents were substantially identical.

An experimental check of one of the variants of the scheme of chromatographic resolution set forth in Fig. 1 was made by us using an artificial mixture consisting of n-butylbenzene, naphthalene,  $\alpha$ -methyl-naphthalene, di-n-butyl sulfide, di-n-nonyl sulfide, isohexylphenyl sulfide\*, di-n-butyl disulfide and benzylmercaptan dissolved in commercial isooctane. The concentration of each component of the mixture was 300 mM/liter. 20 ml of this mixture was brought into ShSM silica gel which was charged into a glass column 1 meter high and 10 mm in diameter. After elution of the adsorbed substances with a mixture of isooctane and acetone (15:1 by volume), three chromatographic filtrates were obtained (No. 1, 2 and 3). Filtrate No. 4, containing benzylmercaptan, was obtained by elution with pure acetone. Filtrate No. 1 was applied to AR carbon in a glass column similar to the one described above. Elution with isooctane gave two filtrates: No. 5 containing n-butylbenzene, and No. 6 containing di-n-nonyl sulfide. Filtrates No. 2 and 3 were chromatogrammed on ASM silica gel to give filtrates No. 7, 8, 9 and 10. Filtrates No. 7 and 10 were chromatogrammed respectively on AR carbon and alumina "for chromatography" to give the filtrates No. 5, 11, 12 and 13. The latter was then chromatogrammed on AR carbon to give filtrate No. 14 which contained isohexylphenyl sulfide in admixture with  $\alpha$ -methyl-naphthalene. The results of the chromatographic operations are detailed in Table 2. These data show the incompleteness of chromatographic separation of our mixture. The comparatively poor yields of isolated components of the mixture is explained by the consumption of the substance for analysis during

The chromatogram shown in Fig. 2 clearly indicates that n-butylbenzene can be satisfactorily separated chromatographically from its mixture with di-n-butyl sulfide, di-n-butyl disulfide and benzylmercaptan. We can therefore assume that it could be recovered from analogous mixtures of organic sulfur compounds. No organic sulfur compounds were detected in the filtrates which contained n-butylbenzene; conversely, n-butylbenzene was absent from the filtrates containing the total sulfur.

TABLE 2

Results of Chromatographic Treatment of an Artificial Eight-component Mixture of Aromatic Compounds and Organic Sulfur Compounds

Mixtures chromatographed	Grade of adsorbents	chromatographic filtrates		
		No.	Composition	yield in % of content in starting mixture
Starting mixture	ShSM	1	—	—
		2	—	—
		3	—	—
Filtrate No. 1	AR	4	benzylmercaptan	72
		5	n-butylbenzene	35
Filtrate No. 2	ASM	6	di-n-butyl sulfide	48
		7	—	—
Filtrate No. 3	ASM	8	di-n-butyl sulfide	21
		9	mixture of naphthalene and di-n-butyl sulfide	81 (disulfide)
Filtrate No. 7	AR	10	—	—
		11	n-butylbenzene	60
		12	di-n-butyl sulfide	traces
Filtrate No. 10	Al <sub>2</sub> O <sub>3</sub>	13	mixture of naphthalene and di-n-butyl sulfide	—
		14	di-n-butyl sulfide	24
Filtrate No. 13	AR	15	mixture of $\alpha$ -methylnaphthalene and isohexylphenyl sulfide	—

As in the preceding experiment, we see that the magnitude of the specific adsorption obtained under the experimental conditions does not always unequivocally characterize the degree of resolution of the chromatographed substances nor the order of their elution, and that the adsorbed substances exert a reciprocal influence. Thus, for example, judging by the magnitude of the specific adsorption on ASM silica gel, it was to be expected that n-butylbenzene would be difficultly separable from di-n-butyl disulfide. The experiment shows, however, that n-butylbenzene is eluted in the pure form and that di-n-butyl disulfide is eluted after discharge of the n-butylbenzene.

Under conditions similar to those employed in the experiments with the artificial mixtures, the chromatographic process was applied to a mixture of aromatic hydrocarbons and organic sulfur compounds separated from the 194-214° fraction of Tuimazin petroleum (Fig. 3). The curves indicate that a considerable proportion of the aromatic hydrocarbons is separated without contamination with organic sulfur compounds. It should be noted that in a filtrate whose refractive index was 1.4048, no organic sulfur compounds were present, and the formolite reaction was positive (confirmation of isolation of aromatic hydrocarbons free of organic sulfur compounds).

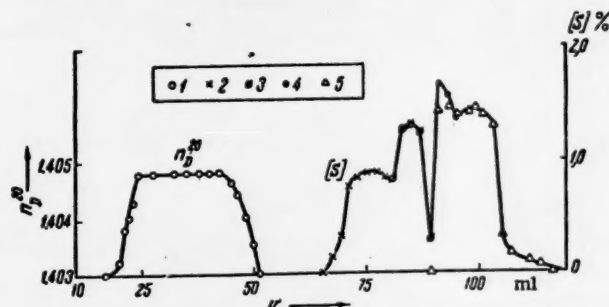


Fig. 2. Chromatogram of an artificial mixture of n-butylbenzene and organic sulfur compounds on ASM silica gel: 1) n-butylbenzene, 2) n-dibutyl disulfide, 3) n-butyl sulfide, 4) mixture of sulfide and mercaptan, 5) benzylmercaptan.



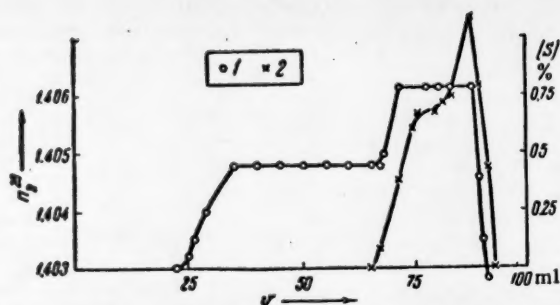


Fig. 3. Chromatogram of mixture of aromatic hydrocarbons and organic sulfur compounds isolated from the 194-214° fraction of Tuimazin petroleum. Adsorbent: ASM silica gel. 1)  $n_D^{20}$ , 2) total sulfur.

The results of chromatographic treatment both of the artificial mixtures and of the narrow fraction separated from sulfur-containing petroleum indicate the possibility in principle of chromatographic resolution of mixtures of aromatic hydrocarbons and organic sulfur compounds. They also point to the need for further systematic investigation of this problem.

Assistant G.P. Gribkova participated in the experimental work.

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## TWO METHODS FOR THE TECHNICAL SYNTHESIS OF METHYLPENTADIENE

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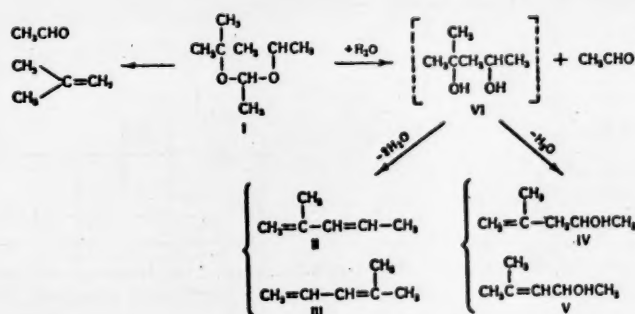
(Presented by Academician L.N. Nazarov, January 15, 1957)

Methylpentadiene is a diene which up to now has not been readily accessible. The only method of possible industrial value is a three-stage method starting from acetone which was proposed by American authors [1]. Methylpentadiene is of definite technical interest due to the properties of its polymers and copolymers [2]. In the present paper we describe two methods of technical synthesis of methylpentadiene that we have developed.

1. A close examination was made in our laboratory of the reactions of olefins with aldehydes [3]. The main product of the reaction of isobutylene with acetaldehyde, even in presence of 1-2% sulfuric acid, is 2,4,4,6-tetramethyl-1,3-dioxane [TMD (I)]; the latter is obtained in a yield of 90% reckoned on the aldehyde reacted. Reference is made in the literature to the use of alkyl-1,3-dioxanes as starting substances for the synthesis of dienes [4].

Our experiments showed that passage of TMD (I) in admixture with steam at a temperature of 300-325° over a catalyst gave methylpentadiene in a yield of up to 75 mole-% on the reacted I. The reaction gives two isomeric dienes: 2-methylpentadiene-1,3 (II) and 4-methylpentadiene-1,3 (III), which have very similar physical properties. Their quantitative determination in the mixture is based on the difference in behavior towards maleic anhydride; II forms an adduct while III forms a copolymer [5]. The susceptibility of III to polymerization can be suppressed by inhibitors, and it can then be separated from II. II and III were obtained in a ratio of 45:55.

Apart from methylpentadiene, the catalytic reaction also gives a small amount (3% on the I passed) of a mixture of two isomeric methylpentenols (IV and V). I is also cracked to some extent to form the original acetaldehyde and isobutylene. We consider the following reaction scheme to be probable for the catalytic breakdown of TMD (I) to a diene:



Water evidently participates in the reaction and promotes the hydrolysis of I at the surface of the catalyst to form the intermediate diol (VI). In the instant of its formation, the latter is dehydrated with splitting-out of one or two molecules of water with formation respectively of a mixture of the two isomeric methylpentenols

(IV and V) or the dienes (II and III).

In Table I are presented the data of one of the typical experiments for establishment of the material balance of the process of catalytic degradation of L. Reaction conditions: temperature 325°, space velocity 2.63, dilution with steam 1:3. The amount of I taken was 47.67 g.

TABLE 1

	Yield in g on I passed	Yield in mole-%	
		on the I passed	on the I reacted
Methylpentadiene	18.6	68.6	74.4
Isobutylene	3.28	17.7	19.2
Butylenes and propylene	0.27	1.4	1.5
Carbon on catalyst	0.052	0.2	0.2
Dioxane	2.3	4.8	—
*recovered*	1.01	3.0	—
Methylpentenol	2.16	4.3	4.7
Resin and losses			
<b>Total</b>	<b>47.67</b>	<b>100.0</b>	<b>100.0</b>

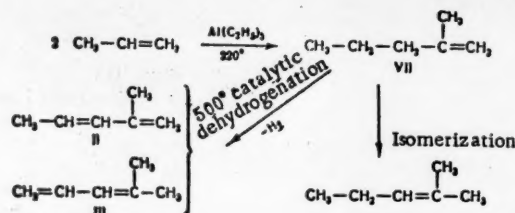
TABLE 2

	Yield in (in g) on VII consumed	Yield in mole %	
		on VII passed through	on VII decomposed
Methylpentadiene	24.152	37.0	71.4
Isoprene	1.160	1.8	3.4
Isobutylene	2.210	3.4	6.5
Propylene	0.880	1.3	2.5
*Recovered* dimer	31.260	—	—
Higher hydrocarbons	0.930	1.4	2.7
Carbon on catalyst	1.725	2.6	5.0
Losses	2.883	4.4	8.6
<b>Total</b>	<b>65.2</b>	<b>—</b>	<b>100.0</b>

II. Another possible technical method of synthesis of methylpentadiene is the dehydrogenation of propylene dimer - 2-methyl-1-pentadiene (VII). This dimer can be prepared in nearly quantitative yield by dimerization of propylene by Ziegler's method [6] in presence of a trialkylaluminum as catalyst.

Experiments on the catalytic dehydrogenation of VII showed that methylpentadiene (again a mixture of isomers II and III in approximately equal amounts) can be obtained in a yield of 35-38% on the VII passed through and of 70-75% on the VII decomposed.

It is interesting to note that this process is accompanied by considerable isomerization of VII with migration of the double bond to the interior of the molecule and transformation into 2-methyl-2-pentene (VIII). At the same time, VII and VIII are also cracked to a slight extent with formation of isoprene (demethylation), propylene, isobutylene and ethylene:



A typical experiment for establishment of the material balance of the dehydrogenation of 2-methyl-1-pentene (VII) is set forth in Table 2. Experimental conditions: temperature 500°, space velocity 0.6, dilution with steam 1:1.75. 65.2 g of VII was taken into the reaction.

The catalytic reactions were carried out in an electric furnace of the block type with a quartz tube (d = 17 mm, l = 900 mm). The temperatures were measured by thermocouples at the top and bottom of the catalyst bed and were maintained constant to  $\pm 2^\circ$ . The starting products (I and VII) were pressed in through automatic valves in the required ratios, and they first entered a heated vaporizer in which the vapor was brought

to reaction temperature. The gaseous product of reaction passed through a condenser where a large proportion condensed, while the uncondensed material entered a gasholder. The catalyzate was fractionated in a laboratory 33-plate column. The content of dienes in the 50-80° fraction was determined by reaction with maleic anhydride in sealed ampoules [7]. Analysis of the uncondensed gas was performed in an Orsat apparatus, and the content of diene hydrocarbons therein was found with the help of a Bushmarin apparatus [8].

For the material-balance experiments the catalyzate was thoroughly dried and fractionally distilled in a precision 60-plate column.

2,4,4,6-Tetramethyl-1,3-dioxane (I) had b.p. 139-141°;  $d_4^{20}$  0.9039;  $n_D^{20}$  1.4192 (3); the 2-methylpentene-1 (VII) had b.p. 60-62°,  $d_4^{20}$  0.6813,  $n_D^{20}$  1.3920 [9]. Catalytic decomposition of I was carried out in presence of a selective catalyst for the transformation of alkylidioxanes into dienes (developed by one of us jointly with G.I. Kishinsky). Dehydration of VII was effected over a standard catalyst for dehydrogenation of butylene to butadiene (zinc oxide basis).

The space velocity was defined as the number of milliliters of feed of liquid product (of I and VII) per ml of catalyst per hour. Dilution with steam was expressed in ratios by volume of starting products (I and VII) in the liquid form. The mixture of isomeric methylpentadienes had b.p. 75.5-76°,  $d_4^{20}$  0.7215,  $n_D^{20}$  1.4462, hydrogen number found 538-542,  $C_6H_{10}$  calculated 546. Literature data for the mixture of isomers: b.p. 72.5-75.5°,  $n_D^{20}$  1.4474 [10].

**Quantitative determination of II and III.** Into a cooled ampoule containing a weighed amount of maleic anhydride in 5-7 ml toluene was charged a sealed ampoule containing a weighed amount (0.5-0.7 g) of diene with a small admixture of hydroquinone. After sealing the outer ampoule, the inner ampoule was crushed. The system was held for three days at room temperature and then opened. Toluene and unreacted III were taken off in vacuum until the residual weight was constant. M.p. of adduct of II with maleic anhydride, 57.8-58.2°; the literature [5] reports 57°.

**Mixture of isomeric methylpentenols (IV and V).** This was found in the 128-130° fraction on fractional distillation of the "recovered" TMD (Fig. 1). Literature data: b.p. 130-130.5° [11]. Concordant values for the content of IV and V in the fraction were obtained in determination by acetylation and by the bromide-bromate method (for degree of unsaturation); the actual values by the two methods were 75.5 and 76.4%. The acetate prepared had b.p. 142-143° at 742 mm,  $d_4^{20}$  0.8852,  $n_D^{20}$  1.4160,  $MR_D$  40.2, calculated 40.48. Literature data for the acetate of IV [11]: b.p. 150.1° at 763 mm,  $d_4^{20}$  0.8852,  $n_D^{20}$  1.4167.

2-Methylpentene-2 (VIII) was detected on fractionation of the recovered dimer (Fig. 2); b.p. 67-67.5° at 760 mm,  $n_D^{20}$  1.4008,  $d_4^{20}$  0.6896. Literature data: b.p. 67.25° at 760 mm,  $n_D^{20}$  1.4005,  $d_4^{20}$  0.6904 [9].

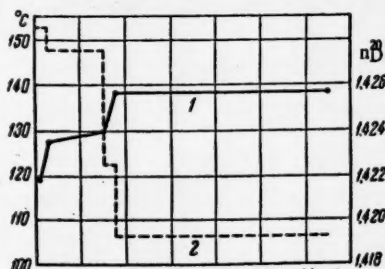


Fig. 1. Plot of distillation of "recovered" tetramethyldioxane: 1) boiling point; 2)  $n_D^{20}$ .

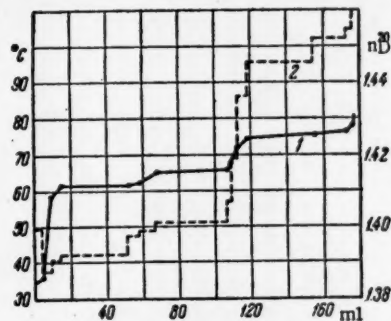


Fig. 2. Plot of fractional distillation of condensate from dehydrogenation of 2-methylpentane-1: 1) boiling point; 2)  $n_D^{20}$ .

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# THE CHEMISTRY OF PIAZOTHIOLE OXIDATION OF 3,4-BENZ-1,2,5-THIODIAZOLE AND ITS DERIVATIVES

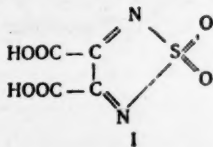
A.M. Khaletsky, V.G. Pesin and Chzhou Tsin

(Presented by Academician I. N. Nazarov, March 12, 1957)

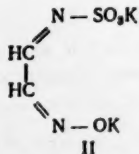
It was earlier shown that piazothiole and its derivatives as well as 1',2'-naphthopiazthiole [1-3], possess a certain degree of unsaturation in addition to aromatic properties; the unsaturated character of these compounds, however, is not devoid of a certain specificity. For example, certain reactions characteristic of olefinic compounds could not be realized with piazothiole (addition of HCl, diene synthesis). Moreover, it was observed that the unsaturation encountered in piazothiole itself is weakened in its 1,4-dichloro derivative; conversely the aromatic character of the latter is intensified. In this connection it was of interest to make further studies of the unsaturated properties of piazothiole and its derivatives. With this objective we made a study of the behavior on oxidation.

Oxidation of piazothiole, 2-methyl-, 2-chloro- and 1,4-dichloropiazthioles led predominantly to breakdown of the whole of the organic portion of the molecule (sulfur was only detected in the form of ammonium sulfate). Apart from ammonium sulfate, the oxidation of 2-chloropiazthiole gives a minute quantity of the 2,4-dinitrophenylhydrazone of (presumably) glycolaldehyde, while the oxidation of piazothiole resulted in only a qualitative indication of the presence of the aldehyde group. Consequently, peracetic acid (which promotes formation of N-oxides of heterocyclic compounds) acts on piazothiole and its derivatives with preferential degradation of the organic portion of the molecule. In this connection it is interesting to note that no appreciable changes are observed when 2-methylpiazthiole is heated with 30% hydrogen peroxide in glacial acetic acid [4].

On oxidation of piazothiole with potassium permanganate, however, we isolated two products: one of them, judging by the analysis and the ability to form a dimetallic derivative, is most probably the S-dioxide of 2,1,3-thiodiazole-4,5-dicarboxylic acid with the structure:



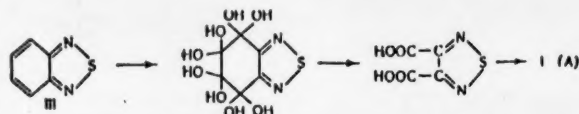
The other was not investigated more closely, but the analysis corresponds to the formula  $C_2H_2N_2O_6SK_2$ , and its structure may possibly be represented by the formula:



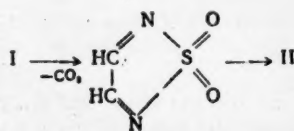
Formation of these substances can be accounted for on the assumption that oxidation with potassium permanganate



goes via preliminary addition of the elements of hydrogen peroxide (Wagner's theory):



Further oxidation of the resultant 2,1,3-thiodiazole-4,5-dicarboxylic acid then occurs at the same time according to the scheme:

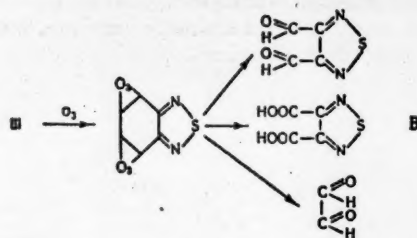


The reaction of oxidation of 2-methyl- and 1', 2'-naphthopiazoles goes in similar fashion.

These ideas about the mechanism of oxidation of plazothiole with potassium permanganate are supported by the oxidation of 1,4-dichloropiazothiole which is much less unsaturated than plazothiole; this observation is in harmony with the behavior on halogenation. Plazothiole itself adds on chlorine or bromine with facility, whereas under analogous conditions 1,4-dichloropiazothiole does not combine with halogens.

1, 4-Dichloropiazothiole reacts much less energetically than plazothiole when it is oxidized with potassium permanganate; it was therefore necessary to perform the reaction under rather more drastic conditions. Process B may then predominate over process A due to which compound II is preferentially formed.

Ozonization of plazothiole\* gave an ozonide with m.p. 60°; after decomposition of the latter, a mixture of 2,1,3-thiodiazole-4,5-dicarboxylic acid, 2,1,3-thiodiazole-4,5-dialdehyde and glyoxal was obtained; in this case the following reaction mechanism may be proposed:



The two last substances were isolated in the form of the respective semicarbazones; in addition a small quantity of ammonium sulfate was obtained.

On the basis of the results of oxidation of plazothiole and some of its derivatives with potassium permanganate and ozone, it follows that plazothiole possesses an unsaturated character, as previously indicated by the results of halogenation.

\* We have to convey our thanks to Prof. A.I. Yakubchik and N.G. Kasatkina for collaboration in the work carried out in the Leningrad State University and for their valuable advice.



## EXPERIMENTAL

Oxidation of plazothiole with peracetic acid. 10 g plazothiole (m.p. 40-42°) and 135 ml acetic acid containing 11% peracetic acid were heated on a boiling water bath for 48 hours, after which the reaction mass was diluted with water. The precipitate (1.3 g of unreacted plazothiole) was filtered off, the filtrate was concentrated (a considerable amount of plazothiole distilled off in this operation) and the residue was washed with alcohol and ether; 0.75 g ammonium sulfate was obtained.

Found %: S 23.75; 23.98 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Calculated %: S 24.24

Oxidation of plazothiole with potassium permanganate. To a mixture of 4 g plazothiole (m.p. 40-42°) and 40 ml water was added, dropwise at 50° and with stirring, 30 g of potassium permanganate (in the form of an 8% solution) until the color was faint pink. The precipitated manganese dioxide was filtered off and washed with hot water; the combined filtrates were concentrated in vacuum at 50-60°, after which the crystals were filtered off. 2.42 g of substance was obtained; it contained potassium, was readily soluble in water, poorly soluble in alcohol and insoluble in other organic solvents. The filtrate was neutralized with hydrochloric acid and gave 2.86 g of substance with m.p. 268° (with decomposition); after recrystallization from water it was sparingly soluble in alcohol and insoluble in other organic solvents.

Found %: C 23.70; 23.39; H 1.11; 0.86; N 13.62; 13.68; S 15.23; 15.20 C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>O<sub>6</sub>S. Calculated %: C 23.30; H 0.97; N 13.59; S 15.52

Analysis of the same product in the form of the Ag derivative (gravimetrically): Analysis of the product containing silver:

Found %: Ag 51.80; 51.77 C<sub>4</sub>N<sub>2</sub>O<sub>6</sub>SAg<sub>2</sub>. Calculated %: Ag 51.43

Analysis of the product containing potassium:

Found %: C 10.79; 10.66; H 1.01; 1.19; N 12.12; 12.18 C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>N<sub>2</sub>SK<sub>2</sub>. Calculated %: C 10.53; H 0.89 N 12.28

Oxidation of 1,4-dichloropiazothiole with potassium permanganate. A mixture of 3 g of 1,4-dichloropiazothiole (m.p. 178-179.5°) and 40 ml of 4% sodium hydroxide solution was heated to the boil; at this temperature and with stirring, a solution of 20 g of potassium permanganate in 250 ml water was gradually added until a faint pink coloration appeared. After removal of the manganese dioxide and concentration of the filtrate (in vacuum), 2.32 g of substance was isolated.

Found %: C 10.96; 10.61; H 1.12; 1.05; N 11.93; 12.04 C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>N<sub>2</sub>SK<sub>2</sub>. Calculated %: C 10.53; H 0.887; N 12.28

Ozonization of plazothiole. Ozone (concentration approx. 7%) was passed into a solution of 4 g plazothiole (m.p. 42°) in 65 ml chloroform cooled to -10 to -15° 5 g of white crystals was obtained; m.p. 60° (with decomposition in sealed capillary); yield 73.2% of theory.

1.45 g of the oxonide was decomposed with water and the solution was neutralized with barium carbonate; the precipitate (barium sulfate with excess of barium carbonate) was filtered off and washed with hot water; the combined filtrates were concentrated at 50° in vacuum. The white precipitate was filtered and recrystallized from water to give 0.5 g of the barium salt of 2,1,3-thiodiazole-4,5-dicarboxylic acid.

Found %: C 15.77; 15.48 C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>SBa. Calculated %: C 15.55

The filtrate was diluted with 50° alcohol and to the solution was added 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate; yield 1 g of semicarbazone with m.p. 193-195°, rising to 196.5-197° after recrystallization from dilute alcohol.

Found %: C 28.09; 28.21; H 3.23; 3.31; N 43.73; 43.41; S 12.40; 12.75 C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>N<sub>4</sub>S. Calculated %: C 28.13; H 3.12; N 43.75; S 12.50

According to the analysis, the compound corresponds to the disemicarbazone of 2,1,3-thiodiazole-4,5-dialdehyde.

The aqueous solution of the barium salt (0.5 g) of 2,1,3-thiodiazole-4,5-dicarboxylic acid was treated with sulfuric acid until all the barium was precipitated as sulfate, and the free acid was obtained with m.p. 172-173°.

Found %: N 15.73; 15.90  $C_4H_2O_4N_2S$ . Calculated %: N 16.09

This corresponds to 2,1,3-thiodiazole-4,5-dicarboxylic acid. Another experiment (products of decomposition of 6.4 g oxonide were examined) yielded 0.28 g ammonium sulfate and glyoxal dialdehyde in the form of the semicarbazone.

Leningrad Institute of Pharmaceutical Chemistry

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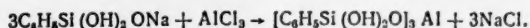
# SYNTHESIS OF POLYORGANOALUMINOSILOXANES THE DOUBLE DECOMPOSITION REACTION OF THE SODIUM SALTS OF ALKYLSILANETRIOLS WITH ALUMINUM CHLORIDE

Acad. Sci. USSR Corresponding Member K. A. Adrianov and A. A. Zhdanov

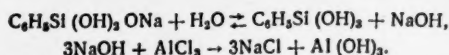
Methods are known in the literature for the preparation of polymers containing together with silicon and oxygen atoms, metal atoms in the main chain. Thus, for example, methods are described for the preparation of polyorganoaluminosiloxanes [2], polyorganotitanosiloxanes and polyorganotin siloxanes [3]. These polymers were synthesized by the joint hydrolysis of the halide or alkoxy derivatives of the corresponding metals and the alkyl- or arylhalosilanes.

In the present investigation our problem was to make a study of the reaction of the sodium salts of alkylsilanetriols with aluminum chloride.

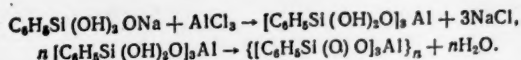
As is known, in their properties the sodium salts of the alkylsilanetriols are similar to the salts of weak organic acids. It was to be expected that the reaction of these salts with aluminum chloride would lead to double decomposition in accord with the scheme:



The formation of polyorganoaluminosiloxanes by reaction (A) will to a large extent be determined by the conditions of running the process. If a substantial amount of water is present in the reaction medium, then the process should go in the direction of forming aluminum hydroxide:

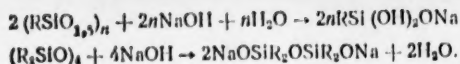


An anhydrous medium should facilitate progress of the process in accord with scheme (A), since of the four components found in the system the first three are soluble in organic solvents, while the sodium chloride is insoluble. Our investigations revealed that the reaction of aluminum chloride with the sodium salts of phenylsilanetriol and ethylsilanetriol and with the disodium salt of 1,3,5-triphenyl-1,3,5-trimethyltrisiloxane proceeds with the formation of polyorganoaluminosiloxanes in accord with the scheme:



The obtained polymers are hard brittle glassy substances, soluble in benzene, alcohol and acetone. Transparent films are formed when their solutions are allowed to evaporate on hard surfaces.

The sodium salts of the alkylsilanetriols used by us for the double decomposition reaction were synthesized by reacting equimolar amounts of sodium hydroxide and the polyorganosiloxane in accord with the scheme:



The sodium salts of the alkylsilanetriols are hard crystalline substances, containing water of crystallization. The amount of the water depends on the recrystallization conditions, the nature of the solvent used in the recrystallization, and the method of drying the salt. Depending on the amount of crystallization water these substances are soluble in alcohol and acetone.

## EXPERIMENTAL

**Sodium salt of phenylsilanetriol.** A solution of 106 g (0.5 mole) of phenyltrichlorosilane in 100 ml of ether was hydrolyzed with a mixture of 200 ml of water and 100 ml of ether. After hydrolysis the organic layer was separated, washed, dried over sodium sulfate, and the diethyl ether was distilled on the water bath. The obtained polymer was dried at 60–80° in a thermostat, after which it was treated with 100 ml of a 20% sodium hydroxide solution in ethyl alcohol. On mixing a rise in the temperature of the mixture to 67° was observed and at the same time the polymer dissolved completely in the alcoholic caustic solution. After solution the alcohol was first distilled off on the water bath, and then the solid residue was dried in vacuo up to a temperature of 70° at 25 mm. The dry product was recrystallized from acetone containing 2% water. The obtained needlelike crystals were washed with cold dry acetone, dried in the air for 12 hours, and then in a thermostat at 45–50° until all of the acetone had been removed. The obtained salt contained 11.50% Na and had the composition  $\text{C}_6\text{H}_5\text{Si}(\text{OH})_2\text{ONa} \cdot 1.37\text{H}_2\text{O}$ .

Found %: C 35.52; H 4.88; Na 11.50; Si 14.92. Calculated %: C 35.52; H 4.86; Na 11.34; Si 13.83.

**Disodium salt of 1,3-dihydroxytetramethyldisiloxane.** A mixture of 37 g (0.125 mole) of octamethylcyclotetrasiloxane and a solution of 20 g (0.5 mole) of sodium hydroxide in 50 ml of methyl alcohol was stirred at 40° for 3 hours. On conclusion of stirring the alcohol and unreacted octamethylcyclotetrasiloxane were distilled off, and the solid residue was dried in a drying oven at 130–150°. The obtained white hygroscopic powder was suspended in a double (by weight) amount of dry acetone, water added to the suspension on the basis of 4 moles of water per mole of salt, and the mixture brought to a boil. The undissolved portion was rapidly filtered, the solution cooled, and then treated with an equal volume of benzene. The deposited needle crystals of the salt were dried in the air until all of the solvent had been removed. The obtained salt contained 16.81% Na and had the composition  $\text{NaOSi}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{ONa} \cdot 4\text{H}_2\text{O}$ .

Found %: C 17.26; H 6.89; Si 20.44; Na 16.81. Calculated %: C 17.02; H 7.14; Si 19.87; Na 16.29.

**Sodium salt of ethylsilanetriol.** This salt was obtained by the method described above for the preparation of the sodium salt of phenylsilanetriol. The salt was recrystallized from ethyl alcohol.

Found %: Na 13.68  $\text{C}_2\text{H}_5\text{Si}(\text{OH})_2\text{ONa} \cdot 2\text{H}_2\text{O}$ . Calculated %: Na 13.92.

**Sodium salt of 1,3-5-triphenyl-1,3,5-trimethyltrisiloxane.** This salt was obtained by the method described above for the sodium salt of 1,3-dihydroxytetramethyldisiloxane, from 1,3-5-triphenyl-1,3,5-trimethylcyclotrisiloxane and sodium hydroxide. For reaction we used the recrystallized product.

Found %: Na 9.41  $\text{NaO}[\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{O}]_3\text{Na}$ . Calculated %: Na 9.77.

**Reaction of the sodium salt of phenylsilanetriol with aluminum chloride.** To a solution of 0.075 mole of the sodium salt of phenylsilanetriol in 130 ml of ethyl alcohol was added with stirring a solution of 0.025 mole of aluminum chloride in 35 ml of alcohol. Immediately after adding the aluminum chloride solution, a precipitate began to deposit in the reaction mixture, the amount of which gradually increased. After heating for 10 hours under reflux on the boiling water bath the reaction mass still showed weak alkaline reaction. To completely neutralize the alkali an additional small amount of an alcoholic solution of aluminum chloride was added to the reaction mixture, and the separated sodium chloride was filtered. The total weight of the precipitate was 3.63 g, which analyzed 94.01% sodium chloride, corresponding to a yield of 77.8% of the theoretical. The alcohol was distilled from the filtrate, and during the distillation an additional small amount of sodium chloride deposited, which was also filtered. After all of the alcohol had been removed (at the end under vacuum) the residue was obtained as a hard brittle resin, soluble in organic solvents.

Found %: Si 18.35; Al 7.27;

For the polymer in which the elementary structural unit has the formula  $[C_6H_5Si(O)O]_3Al$ , the calculated Si and Al are respectively 19.20 and 6.15%.

The obtained results are in good agreement with the calculated values.

Reaction of the sodium salt of ethylsilanetriol with aluminum chloride. The reaction was run by the method described above for the sodium salt of phenylsilanetriol. For reaction we took a solution of 0.15 mole of the salt in 225 ml of alcohol and a solution of 0.05 mole of aluminum chloride in 75 ml of alcohol. From the reaction we obtained 7.58 g of sodium chloride, which corresponds to a yield of 86.43% of the theoretical. After distilling off the alcohol we obtained 9.35 g of colorless brittle resin, soluble in organic solvents, the yield of which was 63.53% of the theoretical.

Found %: C 24.45; H 5.79; Si 27.43; Al 8.68

For the polymer in which the elementary structural unit has the formula  $[C_2H_5Si(O)O]_3Al$ , the calculated C, H, Si and Al are respectively 24.48, 5.14, 28.60 and 9.10%.

The obtained results are in good agreement with the calculated values.

Reaction of the sodium salt of 1,3,5-triphenyl-1,3,5-trimethyltrisiloxane with aluminum chloride. The reaction was run by the above described method. For reaction we took a solution of 0.05 mole of the salt in 90 ml of alcohol and a solution of 0.05 mole of aluminum chloride in 60 g of alcohol. From the reaction we obtained 5.38 g of sodium chloride, which corresponds to a yield of 92.1% of the theoretical. After distilling off the alcohol we obtained 20.31 g of the polymer (83.42% of theory).

Found %: C 37.60; H 5.10; Si 21.47; Al 8.84; Cl 1.49

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Academy of Sciences of the USSR

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# PRINCIPLES OF THE CHEMISTRY OF ENZYMES AND ANTIMETABOLITES FROM THE VIEWPOINT OF THE CATALYSIS THEORY

Academician A. A. Balandin

1. Enzymes are colloidal, microheterogeneous catalysts; the catalysis theory has been applied to them at various stages of its development. It is shown below that the multiplet theory [1] is capable of explaining the especially characteristic properties of enzymes, namely their high selectivity and activity. In applying the multiplet theory it is first of all necessary to isolate the index group involved in reaction, i.e. those atoms that react and consequently come in contact with the catalyst atoms (subsequently determined by isotopic methods [1]). The different types of enzymes and their indices are given in Table 1; from this table it can be seen that most enzymatic reactions have either a doublet or triplet index, and that usually the different types of enzymes have different indices. In the indices  $-C$  is different from  $=C$ , and consequently the indices, as an example, for esterases and carbohydrases are different. The indices shown in Table 1 naturally fall into the multiplet classification, with which, as a result, the classification adopted [2] in enzymatology is found to be in agreement. The classification by indices permits improving the existing classification in places, for example, aspartase with its index of  $\begin{smallmatrix} C & C \\ H & N \end{smallmatrix}$  should be excluded from the amidases with their index of  $\begin{smallmatrix} CO \\ NH \end{smallmatrix}$ . In the case of the dehydrases the cleaved H atoms reduce a second molecule, for example indigo, and the reactions are triplet in nature, the same as the decomposition of  $H_2O_2$ .

The methods of examination in the multiplet theory and in the chemistry of enzymes prove to be similar; the active groups of the substrates in the chemistry of enzymes or the pharmacodynamic groups correspond to the indices in Table 1; in them it is the principal valences that participate.

2. Up to ten enzymes of narrower selectivity enter into each type with the same index; this occurs as the result of the influence of extra index substituents (see sections 3 and 4).

3. The same as in catalysis, in enzymatic reactions the substituents exert an influence on the energy of the reactant bonds, found in the index. Thus, the introduction of a methyl group in line with the  $>C=O$  group increases the energy of this bond by 7 kcal. From the equation of the multiplet theory it follows that if the  $>C=O$  bond is found in the index, and if instead of  $CH_3$  the substituent H appears with it, and if here the energy of the C bond with the catalyst remains constant, then the energy of formation of the multiplet complex is diminished by 7 kcal., while the energy of activation of the reaction is decreased by  $\frac{3}{4} \cdot 7 = 5.2$  kcal. Then, in accord with the Arrhenius equation, the velocity constant of the reaction increases 4680-fold at  $37^\circ C$  [ $\log 4680 = 5200/4.57(273 + 37)$ ]. The energy influence exerted by substituents consists in the act of shifting electrons to the energy of the bond in the index.

4. A structural conformity of the substituents gives a finer adjustment. This is shown by the heterogeneous catalysis of optically active substances. By its symmetry a complex of the doublet index group is optically inactive, whereas an optically active catalyst, deposited on an optically active carrier (for example, metal-quartz), selectively accelerates the reaction of one of the optical antipodes from their mixture [3]. From this we conclude that the asymmetric action of a catalyst of enzyme is concentrated, not in the reacting group — the index group, but in the extra index substituents in their superimposition on the carrier in line with the active center as the result of molecular adsorption. This is in agreement with the conclusion made by Klabunovsky and Patrikeeva that the adsorption stage is dissymmetrical, while the catalysis stage is symmetrical [3].

TABLE 1

## Types of Enzymes and Their Indices\*

- 1) Esterases, for example  $\begin{array}{c} \text{(O)=CO} \\ \text{OH} \end{array}$  of cholinesterase,  $\begin{array}{c} \text{PO} \\ \text{OH} \end{array}$  of phosphatases,  $\begin{array}{c} \text{SO} \\ \text{OH} \end{array}$  of sulfatases.
- 2) Carbohydrases, for example  $\begin{array}{c} -\text{C O} \\ \text{(C)-OH} \end{array}$  of maltase. 3) Enzymes of carbohydrate exchange, for example  $\begin{array}{c} -\text{C O}-(\text{P}) \\ \text{OH} \end{array}$  of phosphorylase. 4) Nucleases, for example  $\begin{array}{c} \text{CO} \\ \text{NH} \end{array}$  of nucleosidases. 5) Amidases, for example  $\begin{array}{c} \text{CO} \\ \text{NH} \end{array}$  of urease. 6) Proteolytic enzymes, for example  $\begin{array}{c} \text{(O)=CO} \\ \text{NH} \end{array}$  of pepsin. 7) Oxidative enzymes, containing Fe, for example  $\text{H}_2\text{O}_2$  of catalase,  $\text{H}_2\text{O}_2$  of peroxidase,  $\text{H}_2\text{C:C}^{\text{O:O}}$  of the cytochrome C dihydroxymaleic acid oxidase (complex index). 8) Oxidative enzymes, containing Cu, for example  $\begin{array}{c} \text{CO} \\ \text{H O} \end{array}$ , etc. of tyrosinase.
- 9) Dehydrases  $\text{H}_2\text{C}_2\text{O}_2$   $\text{H}_2\text{A.B}$ . 10) Enzymes, reducing cytochrome c. 11) Yellow enzymes  $\text{H}_2\text{C}_2\text{O}_2$   $\text{H}_2\text{A.B}$ . 12) Nuclein deaminases, for example  $\begin{array}{c} \text{CO} \\ \text{NH} \end{array}$  etc. of guanase. 13) Various oxidases, for example  $\begin{array}{c} \text{CO} \\ \text{OH} \end{array}$  of lipoxidase,  $\text{H}_2\text{C}_2\text{O}_2$  of the dehydrase of aliphatic acids. 14) Desmolases, for example  $\begin{array}{c} \text{CO} \\ \text{CH} \end{array}$  of decarboxylase,  $\begin{array}{c} \text{CO} \\ \text{OH} \end{array}$  of carbonic anhydrase. 15) Hydratases and mutases, for example  $\begin{array}{c} \text{CO} \\ \text{CH} \end{array}$  of fumarase,  $\begin{array}{c} \text{CS} \\ \text{OH} \end{array}$  of coglyoxalase.

\* The dots are bonds. In a doublet reaction two vertical bonds migrate into two horizontal bonds. Some of the characteristic substituents are placed within the parentheses.

In order for such a superimposition of the substituents with their greater van der Waals atomic radii to be possible, it is necessary that a sufficiently large (hollow) recess in line with the active center, on which the atoms of the index show smaller chemical valence radii, be found. The existence of such hollows is supported when the catalytic dehydrogenation of complex molecules—unsymmetrical diphenylethane, various alcohols—and the hydrogenation of triptycene derivatives is studied.

The nature of the hollows is determined from the fact that the carrier, the apoenzyme, is a molecular, protein crystal. In a molecular crystal the molecules show the densest packing, so that the protuberances of one molecule enter into the hollows of a neighboring molecule, being held by van der Waals forces, and also by hydrogen bonds, in which connection the bonding hydrogen does not occupy a particular place. If one molecule is taken out on the surface, then a hollow is formed, repeating to the greatest possible degree (at the points of contact) the shape of the molecule taken out. A different kind of molecule can fit into such a hollow, a portion of which hollow is either similar or close to the shape of the molecule taken out. Such a surface isomorphism is reminiscent of epitaxy [4] (orientes growing together of the crystals of two substances), but differs from it in that due to free rotation around the C-C and other bonds the molecule in the hollow on the surface can assume a different shape than that required for the construction of a new solid phase with epitaxy.

In catalysis with metals at high temperatures the extra index substituents are oriented perpendicular to the catalyst surface, and on oxide catalysts, when H-bonding is possible, the carbon chains of the substituents are arranged parallel to the surface (see the experiments on the dehydrogenation of alcohols over chromium oxide catalyst and the adsorption of alcohols by aluminosilicates).

In Fig. 1 we give a scheme showing the energy levels of molecules in solution (I), of molecules on an active center without adsorption of extra index substituents on the carrier (II), and of the same molecules, but with adsorption of the extra index substituents on the carrier (III). The energy barrier I-II is greater than the I-III barrier, from which the reaction accelerates in I-III. If the adsorbed extra index substituents do not completely fit in their hollow on the surface, then, due to an increase in the distance between molecules, the II-III heat of adsorption decreases. The reaction rate will be greatest when the difference in the II-III levels is at

a maximum, which occurs when the adsorbed portion of the molecule just enters the hollow. The given model explains in principle the high selectivity shown by enzymes. An example of this is the ability shown by cathepsin I of the spleen, acting on amino acids, to hydrolyze peptide linkages in accord with the scheme:

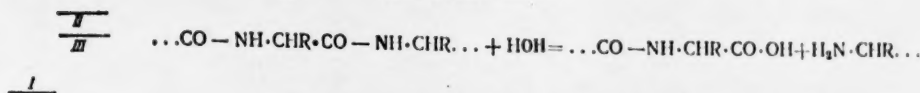


Fig. 1.

(the heavy print indicates the atoms of the index group), only under the conditions that R be either  $\text{HO} \langle \text{---} \rangle \text{CH}_2 -$  or  $\langle \text{---} \rangle \text{CH}_2 -$ . Urease effects the hydrolysis of urea, but not of butylurea — the  $\text{C}_4\text{H}_9$  is incapable of fitting into the same place that H does.

In refining the theory it is necessary to consider the possibility of the oriently adsorbed molecules (which in combination resemble a surface liquid crystal) moving along the surface.

For a long time an especially exact structural relationship between apoenzymes and substituents was established as being a natural assumption in the chemistry of enzymes.

In homogeneous catalysis a molecule of the starting substance can form such a molecular compounds with the catalyst that the molecules of both components in the complex come in contact not only with the reacting atoms, but also with other atoms. The greater speed of reaction of one of the antipodes with the corresponding optically active catalyst is explained in this manner.

Molecular adsorption of substituents in the presence of index groups — surface isomorphism — also serves to explain the especially rapid rate of enzymatic reactions. The molecule is held on the surface of the enzyme in the position necessary for reaction (entropy factor). The adsorption of extra index substituents reduces the energy barrier of the reaction and the value of the adsorption heat (energy factor). Estimating the energy of the H bond as equal to 7 kcal. (average) from a calculation, similar to that given above, we find a 4680-fold acceleration of the reaction. The molecules, adsorbed by the extra index groups, prove to be pressed more strongly by their index atoms to the active centers of the catalytic enzyme which is similar to the effect of a high pressure.

An example of an intermediate complex is shown in Fig. 2. In it the substrate (I), the protein portion of the enzyme (II) and the coenzyme (III) should be in contact with each other, showing good juxtaposition of the protuberances against the hollows. In Fig. 2 for simplicity all of the atoms are taken to be the same and no distinction is made between chemical valence and van der Waals radii. Such a multiplet theory explains the Fischer principle of "a key and lock".

5. Enzyme inhibitors act at different stages of reaction. Strongly adsorbed substances (Hg, HCN, S, etc.) block the active centers of the different enzymes independent of the structure. On the other hand, of a hundred enzymes of one class the antimetabolites may poison only one of them, for the reason that their side chains are adsorbed on the structurally close hollows of the protein portion of the enzymes. As a result, an antimetabolite should have the structure of the group adsorbed on the protein portion of the enzyme, close to the structure of the substrate, and a stronger tendency to be adsorbed in the index group, but it also can contain various substituents (sulfanilamide compounds). The structure of the poisoning group should also not be strongly different from the structure of the index group of the substrate, so that it can fit on the active center of the enzyme. Thus, in p-aminobenzoic acid and in white streptocide the major portions of the molecule are the same ( $\text{NH}_2\text{C}_6\text{H}_4-$ ): The distinguishing groups ( $-\text{COOH}$  and  $-\text{SO}_2\text{NH}_2$ ) are structurally comparable, and their dimensions are close (Fig. 3), in which connection the  $-\text{SO}_2\text{NH}_2$  group is adsorbed more strongly.

Our theory of antimetabolism shows that the theory, considering an antimetabolite as a heterogeneous catalytic poison (Woolley [5]), and the theory, indicating a parallelism between antimetabolism and epitaxy (Erlenmeyer [6]), do not exclude, but instead supplement each other.

Our theory also explains why selective enzyme poisons are frequently prepared from the same enzymes by the procedure of mild chemical reactions. Here the structure of the apoenzyme molecule is retained, but



# THE DEPOSITION OF HALITE IN KARA-BOGAZ GULF

Ya. B. Blyumerg

(Presented by Academician G. G. Urazov, November 12, 1956)

The information characterizing the chemical composition of the Kara-Bogaz Gulf brine at the moment of its saturation with halite is the subject of this paper.

As is known, 1939 proved to be the critical year for the existence of the Kara-Bogaz Gulf: a constant increase in the concentration of the salts in its brine led to the separation of halite in the solid bottom phase on the bottom of the bay. The deposition of halite throughout the whole bay began in early August and was so intense that the screw propellers of the diesel-powered ships, cruising at the time in the bay, were quickly covered with a thick layer of cemented crystals of common salt. Analysis of the brine samples, which were taken at the time of a voyage through the Kara-Bogaz Gulf on August 8-9, 1939 (See Fig. 1), revealed that at the saturation point of the brine with halite the total amount of salts in it was 28.5%, with ~19.7% NaCl. The average value of the chlorine-magnesium coefficient ( $Cl/Mg^{++}$ ) was about 7.25, while the metamorphosis coefficient ( $MgSO_4/MgCl_2$ ) was 1.77. A comparison of the brine composition along a vertical cross section does not show a great difference in the hydrochemical properties of the brine on the surface, in the middle, or at the bottom of the bay (Fig. 2). The actual composition of the Kara-Bogaz brine at the moment of its saturation with halite is in good agreement with the results of the earlier experimental studies [1-5].

TABLE 1

Chemical Characterization of Kara-Bogaz Gulf brine at Its Initial Moment of Saturation With Halite  
(Voyage on the Bay Made August 8-9, 1939)

Date	Station No.	Depth	Specific gravity	Amount of salts (in wt.%)						$MgSO_4/MgCl_2$	$Cl/Mg^{++}$
				$Ca(HCO_3)_2$	$CaSO_4$	$MgSO_4$	$MgCl_2$	$NaCl (+KCl)$	Total salts		
Aug. 8	I	s.	1.234	0.085	0.014	5.45	3.29	19.39	28.23	1.65	7.32
		b.	1.236	0.035	0.014	5.79	3.05	19.45	28.40	1.90	7.25
	II	s.	1.234	0.088	0.041	5.64	3.13	19.90	28.80	1.80	7.42
		b.	1.236	0.086	0.020	5.69	3.21	19.41	28.41	1.77	7.20
	III	s.	1.235	0.086	0.020	5.75	3.09	19.99	28.94	1.86	7.40
		3.5 m	1.238	0.085	0.020	5.65	3.25	19.43	28.43	1.74	7.20
	IV	s.	1.237	0.688	0.007	5.63	3.17	19.92	28.87	1.79	7.36
		b.	1.234	0.090	0.014	5.70	3.13	19.87	28.81	1.82	7.37
	V	3.5 m	1.237	0.085	0.020	5.65	3.25	19.41	28.41	1.74	7.20
		b.	1.235	0.086	0.003	5.68	3.17	19.97	28.91	1.79	7.38
	VI	s.	1.237	0.085	0.013	5.69	3.25	19.33	28.37	1.75	7.15
		3.5 m	1.237	0.085	0.020	5.66	3.29	19.26	28.31	1.72	7.14
Aug. 9	V	s.	1.236	0.077	0.012	5.73	3.09	20.00	28.91	1.85	7.40
		b.	1.234	0.084	0.017	5.59	3.29	19.79	28.77	1.70	7.32
	VI	s.	1.234	0.084	0.017	5.59	3.29	19.79	28.77	1.70	7.32
		3.5 m	1.237	0.085	0.020	5.57	3.41	19.23	28.31	1.63	7.11
	VII	s.	1.237	0.084	0.020	5.64	3.33	19.30	28.37	1.69	7.13
		b.	1.237	0.089	0.003	5.75	3.21	19.84	28.89	1.79	7.29
	VIII	s.	1.237	0.089	0.003	5.75	3.21	19.84	28.89	1.79	7.29
		b.	1.237	0.089	0.003	5.75	3.21	19.84	28.89	1.79	7.29

Note: s. = surface; b. = bottom

The samples of soil, taken at the hydrochemical stations, were found to contain a crystalline solid phase.



The individual crystals, raised from the bottom of the bay together with the slime, represented rhombic dipyramids. The optical constants:  $N_g = 1.982 (\pm 0.002)$ ,  $N_m = 1.477 (\pm 0.002)$  and  $N_p = 1.470 (\pm 0.002)$ , and also the angle of the optical axes ( $2V$ ), close to  $90^\circ$ , left no doubt that the investigated crystals were thenardite. The crystalline crust, raised at the same time from the bottom of the bay, represented a compact mass of fine cemented grains of thenardite with a small inclusion of very fine-grained calcite ( $N_g = 1.658$ )\*.

The formation of the thenardite was due to the dehydration of mirabilite under the influence of a favorable temperature regime ( $27.6^\circ$ \*\*) in the zone of contact between the surface bottom deposits of the bay and the Kara-Bogaz brine, saturated with halite.

Received November 12, 1956

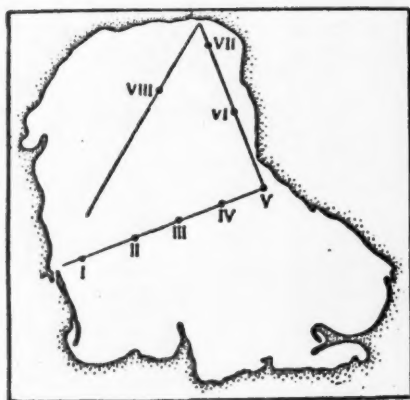


Fig. 1. Location of the Hydrochemical stations in the voyage of August 8-9, 1939.

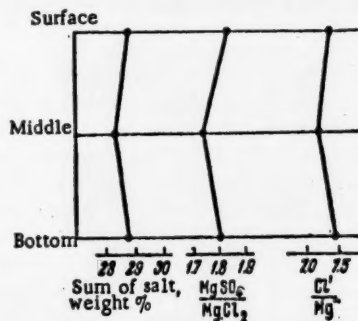


Fig. 2. Hydrochemical cross section of a vertical column of brine in the central portion of Kara-Bogaz Gulf in August, 1939.

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\* The crystallooptical analysis was made by L. O. Anshless and Ya. Yarzhemsky in 1939.

\*\* Average temperature of the brine at the bottom of the bay (from 7 determinations, made at the time of the voyage on August 8-9, 1939).

\*\*\* In Russian.



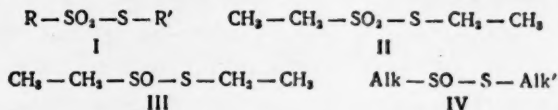
## THE ANTITUBERCULAR ACTIVITY OF ESTERS OF THIOLSUFONIC ACIDS

B. G. Boldyrev, T. S. Ginsburg and R. O. Drabkina

(Presented by Academician L. N. Nazarov, March 12, 1957)

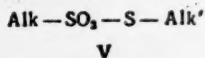
The antitubercular activity of esters I of thiolsulfonic acids has remained completely unstudied up to now; it is only known [1] that the ethyl ester II of ethanethiolsulfonic acid shows bacteriostatic action against *Mycobacterium tuberculosis*, in which connection its activity is equal to that of the analog III of natural antibiotic, namely "allicine."

Taking into consideration the fact that the structure of compounds IV exerts a sharp influence on their antitubercular properties [2], we hoped to find substances with a high antitubercular activity also among the esters I of thiolsulfonic acids.



### Alkyl Esters of Alkanethiolsulfonic Acids

The closest analogs of allicine in their structure are the alkyl esters V of the alkanethiolsulfonic acids, synthesized earlier by one of us together with coworkers [3-6]



with Alk =  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_3\text{H}_7$ ,  $\text{C}_3\text{H}_7\text{-iso}$ ,  $-\text{C}_4\text{H}_9$ ,  $-\text{C}_4\text{H}_9\text{-iso}$ ,  $\text{C}_6\text{H}_5-\text{CH}_2-$   
 Alk' =  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_3\text{H}_7$ ,  $-\text{C}_3\text{H}_7$ ,  $-\text{C}_3\text{H}_7\text{-H}_2\text{O}$ ,  $-\text{C}_4\text{H}_9$ ,  $-\text{C}_4\text{H}_9\text{-iso}$

These compounds show a broad spectrum of antibacterial activity\* and in vitro show bacteriostatic action against gram-positive, gram-negative and acid-resistant bacteria, and against various fungi, protozoa, etc.

**Experiments in vitro.** The study of the antitubercular activity of esters V, done by T. S. Ginsburg and R. O. Drabkina, was made using a 10-12 day old film of a virulent strain of human type No. 32 tuberculosis microbacteria, which was sown on the surface of a Proskauer-Beka culture medium, containing various concentrations of the investigated substances. Similar experiments were made in the presence of 10% horse serum.

The results of the experiments were (taken into account) up to the moment where a good growth of TB appeared in the control test tubes, not containing the compound. The bacteriostatic activity was determined by the smallest amount of investigated substance that gave complete inhibition of TB growth.

\* The antibacterial properties of esters V and VI were studied by V. G. Drobotko, B.E. Aizenman and S. I. Zelepukha in the Institute of Microbiology of the Academy of Sciences of the USSR.

All of the investigated esters showed tuberculostatic action, in which connection the minimum inhibition concentration for most of the compounds ranged in the limits of 1.0-2.0 mg%. The activity of esters V varies within narrow limits and depends but slightly on their structure. Only individual alkyl esters of 2-methyl-1-propanethiolsulfonic acid and butanethiolsulfonic acid show great activity against TB, approaching concentrations as low as 0.01 mg% (1:10 million).

Many of the alkanethiolsulfonic acid esters are inactivated 2-10 times by serum, and some to the extent of 100 and 1000 times. However, all of the methanethiolsulfonic acid and 2-propanethiolsulfonic acid esters completely retain their activity even in the presence of serum, in contrast to the alkyl esters V of the remaining alkanethiolsulfonic acids.

Experiments in vivo. The most active *in vitro* compounds were tested on animals (white mice) to determine their toxicity. The compounds were introduced either subcutaneously or orally once daily. The maximum tolerated dose for most of the tested compounds (with subcutaneous injection for 4-5 days) corresponded to 1 mg. The most toxic compounds — ethyl methanethiolsulfonate and butyl butanethiolsulfonate — produced death of the mice even in dosages of 0.1-0.5 mg.

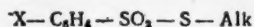
The least toxic substances were tested in experimental tuberculosis to determine their therapeutic activity. For this, a culture of the same TB strain was injected intravenously into white mice in a dose of 0.1 mg. This dose caused death to the animals from tuberculosis in 3-4 weeks after infection. Treatment was begun the next day after implantation and was continued up to the point where the control mice — infected, but not treated — died.

All of the tested esters, even those with maximum *in vitro* activity, proved to be ineffective in curing experimental tuberculosis.

In some cases this can be explained by their ability to be sharply inactivated in the living organism, and in other cases by their great toxicity, not permitting their use in large doses in the *in vivo* experiments.

#### Alkyl Esters of Benzenethiolsulfonic Acid and Its Derivatives

The alkyl esters VI of benzenethiolsulfonic acid and its derivatives [6] show bacteriostatic and bactericidal activity against the same kinds of bacteria that the esters of the alkanethiolsulfonic acids do, but their activity, as a rule, is lower than for compounds V.



with  $X = H-, -p-Cl-, -p-CH_3O-, -p-NO_2-, -p-CH_3CONH-, -p-NH_2-, -m-NO_2-$

$Alk = -C_2H_5-, -C_3H_7-, -C_4H_9-, -C_5H_{11}-iso, -C_4H_9-, -C_6H_{13}-iso$

Experiments in vitro. The antitubercular activity of esters VI was studied by the method described above. Here it was found that they possess a weaker tuberculostatic activity than do the alkyl esters V of the alkanethiolsulfonic acids: a substantial number of them show activity at a concentration of 10 mg% (dilution 1:10,000), while others show activity only at a concentration of 20 mg%. Only individual compounds proved to be more active, but their activity was greatly weakened in the presence of serum.

The introduction of substituents in the *p*-position of the alkyl esters of benzenethiolsulfonic acid changes the activity of the latter but slightly: chlorine and the methoxy group raise the activity slightly, the nitro group is without perceptible influence, while the acetamino group lowers the activity somewhat; the deacylation of the alkyl esters of acetylthiolsulfonic acid exerts a favorable influence, raising the activity of these compounds.

The position of substituents in the benzene ring is evidently not specific for the thiolsulfonic acid esters from the viewpoint of their antitubercular properties: the esters of *m*-nitrobenzenethiolsulfonic acid even exceed the analogous compounds of the *p*-series in their activity.

The same as for esters V, in a number of cases the alkyl esters of benzenethiolsulfonic acid and its derivatives are inactivated by serum, but no sort of relationship between their structure and inactivation was observed.

Experiments in vivo. Three alkyl esters VI, showing *in vitro* activity at a concentration of 1 mg% and not inactivated by serum, were tested for toxicity and in the treatment of experimental tuberculosis in white mice.

The maximum tolerated dose of these compounds was 5 mg. In the treatment of the mice a daily dose equal to 1 mg was used.

Here it was found that the tested compounds do not show therapeutic activity in the living organism.

As a result, the alkyl esters of alkanethiolsulfonic acids, and also of benzenethiolsulfonic acid and its derivatives, show only in vitro tuberculostatic activity, and are without effect in the treatment of tuberculosis in infected animals.

The possibility of using the esters of thiolsulfonic acids in the treatment of external forms of tuberculosis depends on further study.

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Ukrainian Scientific-Research Tuberculosis  
Institute

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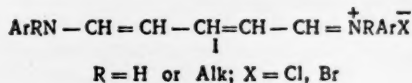
# THE MECHANISM OF CLEAVAGE OF PYRIDINE BASES

A.F. Vompe and N.F. Turitsyna

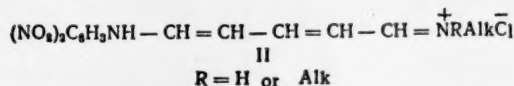
Presented by Academician I. L. Knunyants, February 9, 1957)

The mechanism of the rupture of the pyridine ring has not previously been clarified in spite of the very large number of investigations.

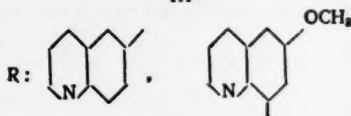
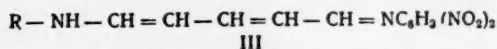
The cleavage of dinitrophenylpyridinium chloride and pyridine cyanobromide by primary and secondary aromatic amines is known to proceed with great velocity and with formation of salts of dianilides of glutaconaldehyde (I) [1]



Reaction of dinitrophenylpyridinium chloride with aliphatic amines (primary and secondary) leads to products of fission of only one nitrogen-carbon bond in the pyridine ring (II) [2].

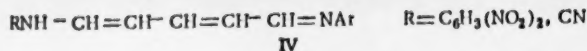


Analogous compounds (III) were isolated by L.L. Knunyants and T. Ya. Kefeli by the action of 6-amino- and 6-methoxy-8-aminoquinoline on dinitrophenylpyridinium chloride [3].

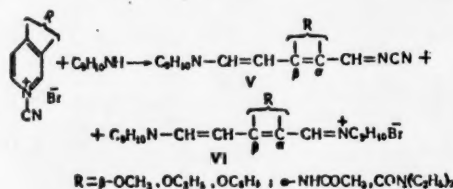


Ebert [6] found that treatment of  $\beta$ -picoline and  $\beta$ -ethylpyridine with cyanogen bromide and aromatic or heterocyclic amines gave cyanoimines of substituted glutaconaldehydes ( $\text{V}; \text{R} = \alpha\text{-CH}_3, \text{C}_2\text{H}_5$ ). None of the cited authors, however, effected the transformation of their products into symmetrical derivatives of glutaconaldehyde with amino residues.

It has therefore not previously been established whether the cleavage of pyridine (especially when the second reactant is an aromatic amine) proceeds via the stage of intermediate formation of compounds (IV) or whether detachment of the nitrogen atom from the pyridine ring occurs in one step due to simultaneous reaction of the cation of the pyridinium salt with two molecules of amine.



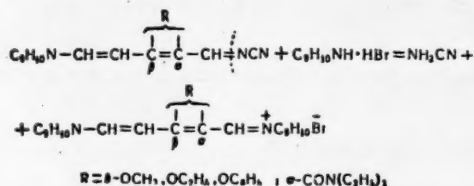
With the objective of investigating the mechanism of rupture of the pyridine ring, we effected cleavage of various derivatives of pyridine bases with cyanogen bromide and tetrahydroquinoline (in acetone or ether solution). We isolated from the reaction mixture, apart from bromides of ditetrahydroquinolides (VI), compounds not containing halogen which proved to be the corresponding cyanoimines (V):



In all cases the main products were cyanoimines. Such a course of the cleavage of substituted pyridines appears to be applicable to pyridine bases in general.

The simultaneous formation in the reaction mixture of cyanoimino derivatives and ditetrahydroquinolides suggests the possibility of cyanoimines being intermediate compounds in this reaction.

It was still not clear, however, why the main products were not the end products of cleavage but the intermediate compounds. In order to demonstrate that cyanoimines are the intermediate products of cleavage, we tried to convert them into symmetrical ditetrahydroquinolides. With this objective, we subjected the cyanoimine to the action of a salt of a second molecule of amine (tetrahydroquinoline hydrobromide). In this manner it was possible under mild conditions (in alcoholic solution with gentle heating or at room temperature) to complete the transition from cyanoimines to symmetrical ditetrahydroquinolides. This reaction takes place comparatively slowly according to the equation:



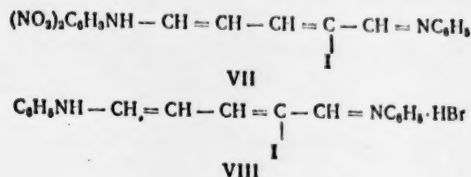
The transition of cyanoimine to ditetrahydroquinolide is particularly conspicuous during cleavage of certain pyridine bases. For example, the reaction of  $\gamma$ -methoxypyridine with cyanogen bromide and tetrahydroquinoline is accompanied by very rapid crystallization of bright yellow crystals of the cyanoimine. The yellow color of the solution then gradually changes to orange and the crystalline mass acquires a heterogeneous appearance due to formation of a mixture of yellow crystals of cyanoimine and orange crystals of ditetrahydroquinolide.

Consequently the cyanoimino derivatives are indeed the intermediate products of rupture of pyridine bases. The preferential formation of cyanoimines on cleavage of substituted pyridines may be attributed to the great speed of rupture of the  $\text{C}_\alpha\text{N}$  bond in the pyridine ring, which exceeds the speed of rupture of the  $\text{C}-\text{N}$  bond in the cyanoimine molecule. If, furthermore, we take into account the poor solubility of chain-substituted cyanoimino derivatives in acetone or ether, it becomes clear why the cleavage is mainly directed towards the formation of cyanoimines.

From these considerations it follows that if the solubility of the cyanoimino derivative could be increased by some means (e.g. by replacing one solvent by another), then the ratio of the substances formed in the reaction mixture might be shifted to favor the ditetrahydroquinolide. It was actually found that by cleavage of  $\gamma$ -phenoxypyridine with cyanogen bromide and tetrahydroquinoline not in a medium of ether (in which the corresponding cyanoimine is poorly soluble) but in acetone, we can obtain solely the bromide of the tetrahydroquinolide of  $\beta$ -phenoxyglutaconaldehyde. It was found that reaction of dinitrophenyl- $\beta$ -iodopyridinium



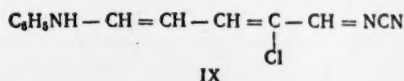
chloride with aniline in a medium of ethyl alcohol gives a good yield of solely the monoanilide of  $\alpha$ -iodo-6-(2', 4'-dinitrophenyl)-amino- $\Delta$ -2,4-pentadienal (VII)



When the reaction is conducted in a medium of methanol (in which the monoanilide VII dissolves more easily), the monoanilide is accompanied by the hydrobromide of the dianilide of  $\alpha$ -iodoglutaconaldehyde (VIII). The failure to isolate the corresponding cyanoimines when pyridine itself is cleaved with cyanogen bromide and amines is evidently due not only to the good solubility of cyanoimines but also to the high speed of rupture of the C-N bond in the cyanoimine.

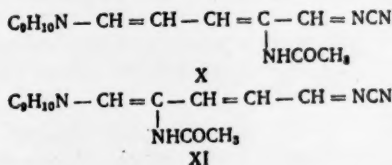
The considerations here developed can readily account for the observations of Dieckmann on cleavage of  $\beta$ -chloropyridine with cyanogen bromide and aniline in ethereal solution [4].

The deep orange precipitate obtained by this reaction contained only a small amount of the hydrobromide of  $\alpha$ -chloroglutaconaldehyde dianilide and consisted mainly of aniline hydrobromide. The yield of the hydrochloride of the dianilide rose sharply when alcohol and aniline hydrochloride were added to the reaction mixture. The accelerating effect of addition of aniline hydrochloride on the cleavage reaction was entirely incomprehensible because aniline hydrochloride is incapable of cleaving pyridine bromocyanide or dinitrophenylpyridinium chloride. The first step in cleavage of  $\beta$ -chloropyridine is evidently the formation of the cyanoimine (IX) which is poorly soluble in ether:



Addition of alcohol and aniline hydrochloride to the reaction mixture leads to partial passage of IX into solution where it reacts with aniline hydrochloride to form the hydrochloride of  $\alpha$ -chloroglutaconaldehyde dianilide.

Two isomers should be expected in the preparation of cyanoimines from  $\beta$ -substituted pyridines. For example, the cyanoimines X and XI could be formed on cleavage of  $\beta$ -acetaminopyridine. Up to now, however, only one isomer has been isolated in any of these reactions. Only one of the  $\text{C}_\alpha\text{-N}$  bonds appears to be preferentially ruptured on cleavage of  $\beta$ -substituted pyridines.



The position of the substituents in these derivatives has not yet been established. It may be suggested, however, that they are in the  $\alpha$ -position to the  $\text{CH}=\text{NCN}$  group.

The cyanoimine of  $\beta$ -methoxyglutaconaldehyde was isolated in two differently colored forms - bright yellow and bright red. Both forms have the same composition and substantially the same melting point. A similar phenomenon was also observed in the case of the cyanoimine of  $\beta$ -ethoxyglutaconaldehyde.

It is known that salts of the dianilides of glutaconaldehydes can exist in two differently colored forms. Zincke attributes the difference in color of these modifications to dimorphism [5]. This explanation might also apply to the cyanolmines discussed above. Consideration must also be given, however, to the possibility of cis-trans isomerism of the cyanolmines. This problem calls for special investigation.

L. V. Ivanova participated in the experimental work.  
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## THE ASSOCIATED STATES OF SELENIUM IN THE GAS PHASE

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(Presented by Academician S. I. Volfkovich, December 25, 1956)

The generally accepted opinion, based on a single investigation of the density of the vapor [1], is that selenium vapor contains two molecular species:  $\text{Se}_2$  and  $\text{Se}_8$ , which are in equilibrium. However, the results of calculations of the equilibria of reactions with participation of elemental selenium, carried out with the help of the data in [1], are at variance with experiment [2].

With the objective of clarifying the problem, we investigated the density of selenium vapor by the static method in a quartz apparatus over the temperature range of 550-900° and over a range of pressures from some tens of millimeters of mercury column to 1 atm.

Use was made of compensation diaphragm gages similar to Brooks' gage [3], with a sensitivity of 0.5-0.1 mm mercury column. The gage and the connection capillary were thermostated at 700°. The reaction vessel (volume approx. 56 ml) was placed in a furnace in the form of a steel block (weight 12.4 kg) with a hole drilled along its axis. In the hole was inserted a quartz tube suspended from the ends of the furnace. The reaction vessel was placed in the tube and retained an unchanged position at a certain observed thermal deformation of the block. The furnace for the thermostating of the manometer was similarly constructed (weight of block 4.2 kg). Each of the furnaces had five independent electrical windings.

The reaction vessel was equipped with four ampoules which enabled five experiments to be carried out with one charge of selenium. The volume of the vessel, ampoules and capillary was determined by calibration with mercury, and that of the gage by calibration with water. The possible error was  $\Delta V_1 \pm 0.02$  ml. Temperatures were measured with a platinum-platinum-rhodium thermocouple (calibrated by us) by the compensation method. Accuracy of measurements  $\pm 1^\circ$ . The temperature in the large furnace was measured at six points by movement of the thermocouple along the sheath sealed to the reaction vessel. The axial gradient did not exceed  $2^\circ$  as a rule. The measurements of pressure with the mercury gage were accurate to  $\pm 0.3$  mm mercury column.

The selenium used in the investigation contained 0.004-0.008% of nonvolatile impurities and 0.001-0.002% of tellurium. It was subjected to eight distillations in high vacuum. It was charged into the reaction vessel by distilling an exactly weighed amount under vacuum in a sealed-off vessel. After charging had been effected, the working part of the apparatus was sealed off from the vacuum part.

The change of pressure with progressive temperature rise of the large furnace is followed from the vapor tension curve. After complete vaporization of the substance, the vapor reaches the zone of the unsaturated state. In our 11 experiments we made 39 measurements in the unsaturated vapor zone which fitted satisfactorily on a single curve. Using the method of least squares, we derived the correlation:

$$\lg P_{\text{mm}} = -\frac{4987.3}{T} + 8.0783. \quad (1)$$

This formula is nearly identical with that of Brooks, which fact is a criterion of the accuracy of our measurements.

Measurements of pressures in the unsaturated vapor region were effected both with rising temperatures and with falling temperatures. The points fit very satisfactorily on the same curves, thereby demonstrating the attainment of equilibrium states.

The values of  $\nu$  (mean number of atoms in a molecule) were calculated from the unsaturated vapor pressures with the help of the equation of state for a gas:

$$\nu_1 = \frac{RT}{AP\nu_1} \left[ m - \frac{PA}{R} \left( \frac{\nu_2\nu_3}{T_1} + \frac{\nu_2\nu_3}{T_3} \right) \right], \quad (2)$$

where the subscripts 1, 2 and 3 refer respectively to the reaction vessel, the manometer and the capillary. The values of  $\nu_2$  and  $\nu_3$  were previously calculated by threefold approximation.

The dependence of  $\nu$  on  $P$  is plotted in Fig. 1. The character of the processes of dissociation in the systems under consideration can be judged from the form of the curves [4-6]. In the case of simple decomposition  $X \rightleftharpoons X_n$  where  $n > 2$ , the curves will be S-shaped, as was shown by Smits [5], and the magnitude of  $n$  can be determined from the position of the inflexion point on these curves. Our experimental data do not clearly indicate the position of the inflexion point on the  $\nu$ - $P$  isotherms. Qualitatively the character of our curves is consistent with the generally accepted ideas [1]. However, the constants of the simple dissociation  $Se_6 = 3Se_2$  calculated from the formula (Table 1)

$$K = \left( \frac{6-\nu}{4} P \right)^3 : \frac{\nu-2}{4} P, \quad (3)$$

reveal at high temperatures a tendency to rise with increasing  $P$ . This rise exceeds the possible deviations  $\Delta K$  which are easily evaluated by calculating the values of  $\Delta\nu$ . In calculating  $\Delta\nu$  from equation (2) we assumed the above-stated accuracies of measurement of  $P$ ,  $T_1$  and  $\nu_1$  and we attained accuracies of measurements of  $T_2$  and  $T_3$  of  $\pm 10$  and  $\pm 20^\circ$ . We neglected the errors of  $\Delta m_3$ ,  $\Delta\nu_2$  and  $\Delta\nu_3$  due to their smallness; the value of  $\Delta\nu_2$ , evaluated separately for each point from a special graph, was of the order of  $\pm 0.1$ . We assigned a value of  $\pm 0.00004$  g to the error in the determination of the total mass  $\Delta m$  for the first and last experiment of each series, while we assigned values of  $\pm 0.00012$  and  $0.00009$  g (half of the differences between the original weights and the totals of the sealed-off masses of selenium) for the intermediate experiments.

The fall in the constants with falling pressure testifies to the presence of an associated stage of selenium intermediate between  $Se_2$  and  $Se_6$ .

If the dissociation  $Se_6 \rightleftharpoons Se_4 + Se_2$  is assumed, then we have  $(6-\nu)P:4 = P_2 + P_4:2$  and  $(\nu-2)P:4 = P_6 + P_4:2$ , where  $P_2$ ,  $P_4$  and  $P_6$  are the partial pressures of the respective associated forms. Hence the constant calculated from equation (3) is actually:

$$K = \frac{P_2(2 + K'_4P_2)^3}{4(K'_4 + 2K'_6P_2)}, \quad (4)$$

where  $K'_4 = P_4:P_2^2$ , and  $K'_6 = P:P_2^2$ .

It follows from equation (4) that the constant must become larger with rise of  $P_2$  in proportion to the total pressure, and this occurs in the case considered. It is easy to show that if  $Se_3$  had been present in the system in addition to  $Se_2$  and  $Se_6$ , the constants would have become smaller.

A theoretically founded method of calculation of the constants of the complex equilibria requires knowledge of the dependences of  $\nu$  on  $P$  at  $P \rightarrow 0$ . In our case such a calculation would have involved excessively arbitrary extrapolations. We therefore made use of the method of selection in which account is taken of the values of the constants determined when calculating the simpler decomposition. Only the 700-900° isotherms satisfactorily describe the constants of the three-stage dissociation. All the isotherms satisfactorily describe the constants of the four-stage dissociation, in harmony with the unchanged value of the constants of

simple dissociation  $\text{Se}_6 \rightarrow \text{Se}_2$  for the temperatures of 550 to 650° at which the influence of  $\text{Se}_4$  molecules is offset by the influence of  $\text{Se}_8$ .

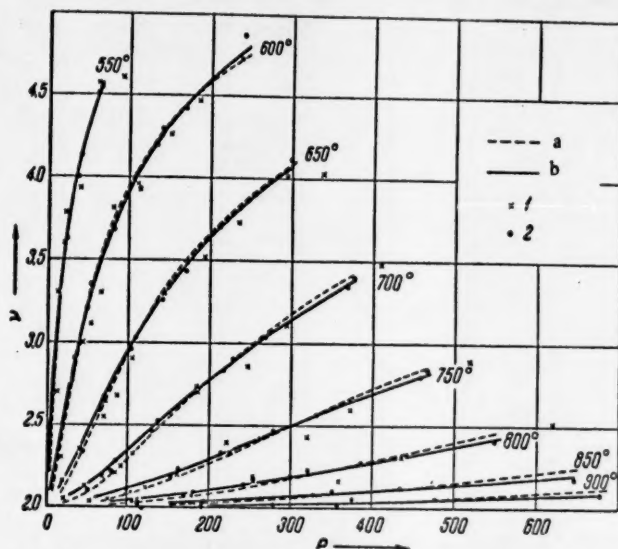


Fig. 1.  $\nu$  as a function of  $P$ ; a) for complex decomposition, b) for simple decomposition; 1) experimental points of Preuner and Brockmoller [1], 2) authors' experimental points

In selecting the constants of the four-stage dissociation, analogous to the dissociation of sulfur vapor [7], we arbitrarily assumed the thermal effects to be independent of the temperature, which is of course not perfectly correct.

The dependences of  $\log K$  on  $1/T$  are represented by the equations:

$$\lg K_4 = -\frac{36700}{4.576 T} + 11.31; \quad \lg K_6 = -\frac{62700}{4.576 T} + 19.23;$$

$$\lg K_8 = -\frac{93900}{4.576 T} + 29.41.$$

The too large value of  $\Delta H$  in the first equation is somewhat questionable. The calculated dependences of  $\nu$  on  $P$  are shown in Fig. 1 (continuous lines for complex and broken lines for simple dissociation). The latter are calculated from the average-weighted constants of Table 1. Special note should be taken of the considerable scatter of the points of Preuner and Brockmoller with rising pressures in the very region where the accuracy ought to have been greater.

The authors are deeply grateful to S. L. Volfkovich, in whose laboratory the investigation was undertaken, for his constant interest and support.

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TABLE 1  
Dissociation Constants of Simple Decomposition

550°				600°				650°				700°			
P	v	$\Delta v$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$	P	v	$\Delta v$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$	P	v	$\Delta v$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$	P
57.0	4.553	$\pm 0.050$	3.31	$\pm 0.40$	170.2	4.414	$\pm 0.025$	2.99	$\pm 0.17$	298.2	4.113	$\pm 0.023$	1.77	$\pm 0.08$	357.9
62.8	4.506	$\pm 0.050$	3.30	$\pm 0.40$	142.5	4.288	$\pm 0.024$	2.79	$\pm 0.19$	294.2	4.018	$\pm 0.019$	2.09	$\pm 0.08$	369.3
41.6	4.125	$\pm 0.050$	3.35	$\pm 0.35$	134.8	4.192	$\pm 0.024$	3.13	$\pm 0.16$	212.6	3.702	$\pm 0.021$	2.01	$\pm 0.08$	288.6
38.8	4.062	$\pm 0.072$	3.76	$\pm 0.54$	110.3	4.017	$\pm 0.034$	2.94	$\pm 0.20$	180.6	3.548	$\pm 0.027$	1.94	$\pm 0.10$	229.6
26.5	3.617	$\pm 0.065$	3.69	$\pm 0.45$	85.7	3.751	$\pm 0.036$	2.99	$\pm 0.21$	171.8	3.436	$\pm 0.022$	2.16	$\pm 0.09$	216.5
					81.2	3.770	$\pm 0.040$	2.92	$\pm 0.23$	142.7	3.040	$\pm 0.020$	2.16	$\pm 0.11$	179.2
					81.2	3.770	$\pm 0.040$	2.92	$\pm 0.23$	142.7	3.040	$\pm 0.020$	2.16	$\pm 0.11$	179.2
					50.9	3.213	$\pm 0.034$	2.91	$\pm 0.26$	105.4	2.952	$\pm 0.033$	2.02	$\pm 0.11$	139.5
					34.7	2.966	$\pm 0.046$	2.44	$\pm 0.23$	70.9	2.670	$\pm 0.026$	1.73	$\pm 0.11$	86.4
										66.1	2.586	$\pm 0.036$	1.85	$\pm 0.17$	80.3
										44.9	2.349	$\pm 0.035$	1.77	$\pm 0.23$	52.4
$\bar{K} = 3.44 \cdot 10^3$				$\bar{K} = 2.86 \cdot 10^3$				$\bar{K} = 1.96 \cdot 10^3$				$\bar{K} = 1.08 \cdot 10^3$			
750°				800°				850°				900°			
P	v	$\Delta v$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$	P	v	$\Delta v$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$	P	v	$\Delta v$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$	P
465.0	2.846	$\pm 0.017$	5.03	$\pm 0.17$	543.2	2.415	$\pm 0.015$	2.12	$\pm 0.10$	625.9	2.188	$\pm 0.014$	7.36	$\pm 0.66$	678.7
457.5	2.799	$\pm 0.015$	5.36	$\pm 0.18$	385.7	2.278	$\pm 0.017$	1.72	$\pm 0.13$	427.3	2.128	$\pm 0.017$	5.08	$\pm 0.71$	456.3
331.2	2.566	$\pm 0.018$	4.90	$\pm 0.23$	320.2	2.234	$\pm 0.021$	1.47	$\pm 0.16$	351.3	2.110	$\pm 0.021$	4.11	$\pm 0.86$	374.6
279.3	2.474	$\pm 0.022$	4.51	$\pm 0.29$	299.4	2.194	$\pm 0.019$	1.60	$\pm 0.19$	265.8	2.081	$\pm 0.019$	4.97	$\pm 1.23$	277.8
292.0	2.425	$\pm 0.018$	4.62	$\pm 0.27$	242.4	2.147	$\pm 0.022$	1.43	$\pm 0.24$	193.3	2.038	$\pm 0.023$	4.57	$\pm 1.83$	203.2
214.4	2.340	$\pm 0.023$	4.15	$\pm 0.36$	180.3	2.097	$\pm 0.023$	1.24	$\pm 0.31$	160.8	2.032	$\pm 0.024$	4.57	$\pm 1.83$	193.0
163.0	2.227	$\pm 0.024$	3.90	$\pm 0.48$	169.5	2.072	$\pm 0.025$	1.49	$\pm 0.57$	111.6	2.027	$\pm 0.026$	4.57	$\pm 1.83$	117.1
154.0	2.196	$\pm 0.024$	4.19	$\pm 0.58$	103.9	2.032	$\pm 0.020$	1.37	$\pm 0.64$	102.0	1.983	$\pm 0.021$	4.57	$\pm 1.83$	106.8
98.0	2.105	$\pm 0.020$	3.34	$\pm 0.72$	89.5	2.035	$\pm 0.023$	1.37	$\pm 0.64$						
89.9	2.063	$\pm 0.025$	4.30	$\pm 1.87$	61.2	1.965	$\pm 0.025$	1.37	$\pm 0.64$						
$\bar{K} = 4.86 \cdot 10^3$				$\bar{K} = 1.78 \cdot 10^3$				$\bar{K} = 5.65 \cdot 10^2$				$\bar{K} = 1.39 \cdot 10^2$			

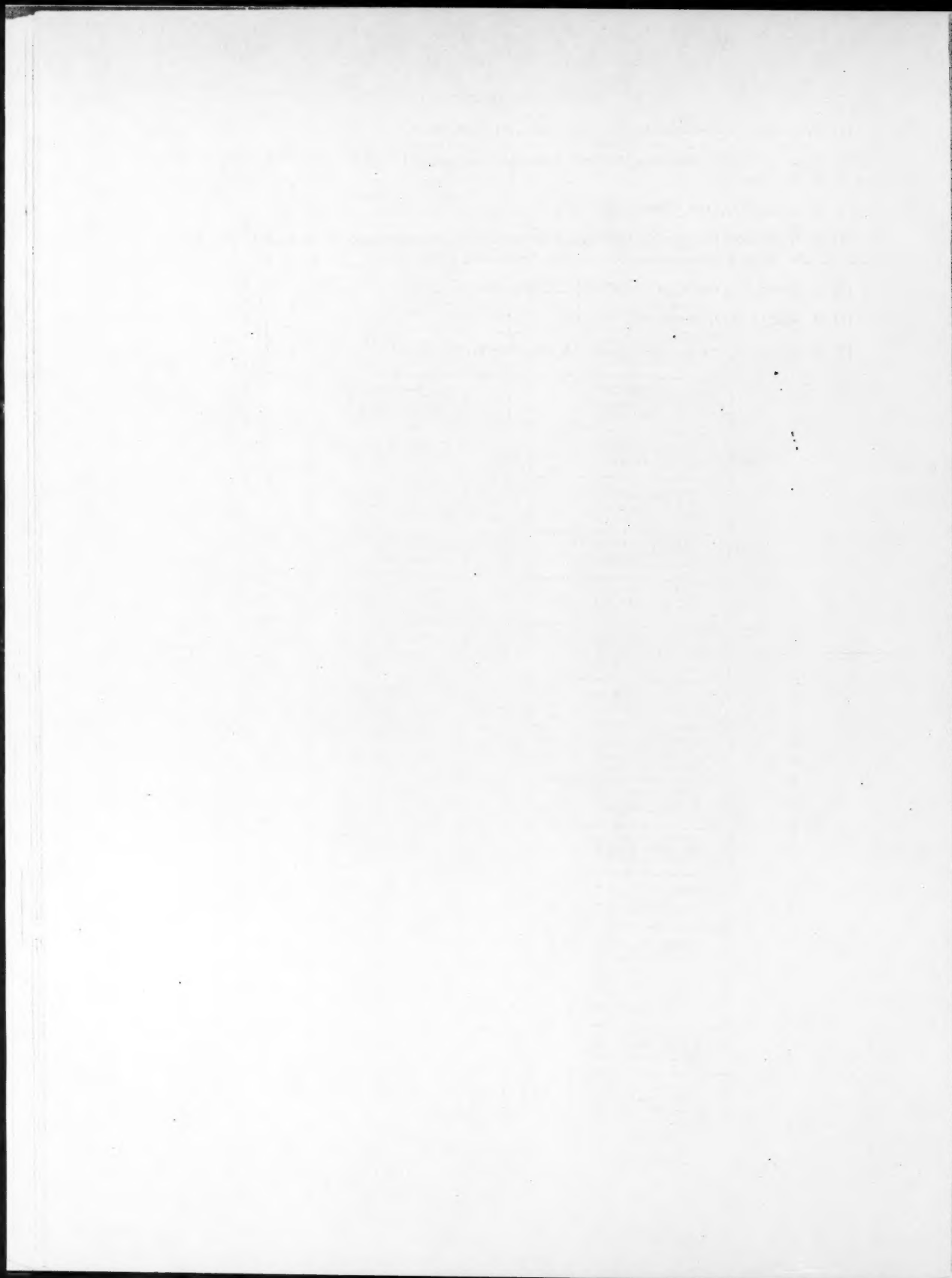
\* Calculation of these constants was pointless due to the large values of  $\Delta K$ .



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# THE ACTION OF ACID CHLORIDES OF INORGANIC ACIDS ON ARYSULFONIC ACIDS

## A GENERAL METHOD FOR THE PREPARATION OF ANHYDRIDES BY THE REACTION OF ACIDS WITH $P_2O_5$

V.O. Lukashevich

(Presented by Academician B. A. Kazansky, February 23, 1957)

It is well-known that the most usual methods for transformation of arylsulfonic acids into sulfochlorides are based upon treatment of sodium or potassium salts of sulfonic acids with phosphorus pentachloride. Phosphorus oxychloride is used more rarely. Chlorosulfonic acid is usually brought into direct reaction with the unsulfonated substances. Among other acid chlorides, such as  $PCl_3$ ,  $SOCl_2$  and  $COCl_2$  (some of which are incidentally used extensively for the preparation of acid chlorides of carboxylic acids), thionyl chloride is the most widely used. According to Hans Meyer [1], boiling of thionyl chloride with sulfonic acids or their salts frequently leads to formation, apart from the sulfochlorides, of the anhydrides of the sulfonic acids; in the opinion of the author, sulfochlorides and anhydrides are formed in the main independently of one another.

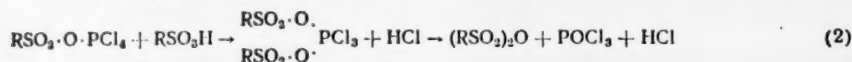
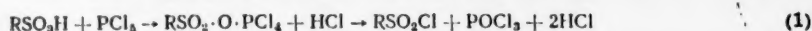
Judging by the literature, in exceptional cases the formation of anhydrides is also possible by the interaction of sulfonic acids with phosphorus pentachloride. This occurs, for example, in the case of p-xylene-o-disulfonic acid [2] and of p-difodobenzene-sulfonic acid [3]. On the basis of our observations, however, it appears that the formation of anhydrides by the action of phosphorus pentachlorides on sulfonic acids or their salts is of fairly common occurrence the results obtained with a number of compounds in this reaction are given in Table 1.

TABLE 1

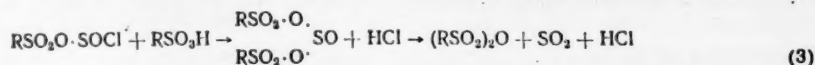
Experiment No.	Radical of the sulfonic acid	Experiments with sulfonic acids			Experiments with Na salts of sulfonic acids		
		Duration of experim. (min.)	Anhydride % of theory	Sulfochloride % of theory	Duration of exp. (min.)	Anhydride % of theory	Sulfochloride % of theory
1	4-Cl-C <sub>6</sub> H <sub>4</sub> -	5	5.4	83.0	5		93.0
2	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	—	—	—	15	7.3	90.0
3	2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	5	59.3	33.0	10	8.1	85.0
4	2,3,5,6-Cl <sub>4</sub> C <sub>2</sub> H-	5	40.7	55.4	90		98.5
5	2,4-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	5	38.2	49.3	15	5.8	91.8
6	2,5-Br <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	5	34.7	62.2	20	3.3	18.5
7	3-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> -	5	25.3	62.7	10	none	53.9
8	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	5	16.6	73.9	5		97.9
9	2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	5	38.1	60.1	5	15.2	84.6
10	2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	2	28.0	64.2	5	1.0	84.0
11	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> -	3	61.6	29.4	6	34.0	60.4

The sulfonic acid (0.01 mole), usually containing one mole of water of crystallization, or the corresponding amount of anhydrous sodium salt is wetted with phosphorus oxychloride (1 ml) and immediate addition is made of  $PCl_3$  in powder form (4 g). An energetic reaction commences in the case of a number of sulfonic acids, the mass reaches a temperature of 35-40° and liquefies. The sodium salts react more slowly (see experiments 4, 6 and 7). After expiration of the period specified in the table, the semiliquid mass is poured into a beaker containing ice and vigorously shaken. The solidified, triturated product is filtered, washed with

water and dried on a funnel through which air is drawn at room temperature. The anhydride and the sulfochloride are separated with the help of glacial acetic acid or ether (the anhydride is sparingly soluble in these solvents). We satisfied ourselves that the anhydrides of the sulfonic acids are formed before treatment of the reaction mixtures with water. If for example, in experiment 3 (with sulfonic acid) the mass is diluted with a small quantity of  $\text{POCl}_3$  (2 ml), filtered and washed with absolute ether, then the amount of anhydride obtained is about 40% of theory. Moreover, the anhydrides of the sulfonic acids are hardly changed after short-period action of  $\text{PCl}_5$  in admixture with  $\text{POCl}_3$  (10 min,  $30^\circ$ ). Finally, under these conditions the possibility is excluded of formation of anhydrides of sulfonic acids by the action of sulfochlorides on sulfonic acids or their salts (method for preparation of anhydrides of carboxylic acids). We can therefore assume that the mechanism of formation of sulfochlorides and anhydrides of sulfonic acids, starting from the sulfonic acids and their salts, is represented by the following schemes:



An analogous mechanism is applicable to the formation of sulfonic acid anhydrides in the reaction with thionyl chloride:



These equations reflect the fact that the process of "transanhydridization" (in our cases the transition from acid chlorides of inorganic acids to acid chlorides or anhydrides of arylsulfonic acids) is realized through the corresponding mixed anhydrides (in a similar manner to the formation of acid chlorides and anhydrides of carboxylic acids).

Phosphorus oxychloride reacts very much more slowly than  $\text{PCl}_5$  with free sulfonic acids and their sodium salts; the products in the case of the salts are exclusively sulfochlorides, whereas anhydrides are also often formed in addition when the sulfonic acids are used (Table 2). In all of the experiments the sulfonic acid (0.01 mole), containing 1 or 2 moles of water of crystallization, was heated for 1 hour with  $\text{POCl}_3$  (4 ml) at  $104-106^\circ$ , after which the mixture was cooled and decomposed with iced water as described above.

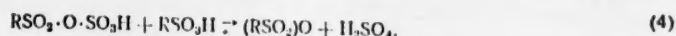
TABLE 2

Experiment No.	Sulfonic acid radical	with $\text{POCl}_3$			With $\text{PCl}_5$		
		Anhydride % of theory	Sulfochloride % of theory	Duration of exp. (hrs.)	Anhydride % of theory	Sulfochloride % of theory	
1	$\text{C}_6\text{H}_5-$	20.0	68.0	2	28.2	2.3	
2	$4\text{-ClC}_6\text{H}_4-$	40.2	41.8	2	32.7	3.0	
3	$2,5\text{-Cl}_2\text{C}_6\text{H}_3-$	66.5	18.8	2	10.5	traces	
4	$3\text{-(NO}_2\text{)C}_6\text{H}_3-$	51.5	13.5	2	9.0		
5	$2,4\text{-(CH}_3\text{)}_2\text{C}_6\text{H}_3-$	—	98.0	1	40.0	•	
6	$2,4,6\text{-(CH}_3\text{)}_3\text{C}_6\text{H}_2-$	—	98.5	1	63.0	7.4	
7	$\text{C}_{10}\text{H}_7-1-$	—	98.0	1	42.5	10.2	
8	$\text{C}_{10}\text{H}_7-2-$	—	86.5	1	38.5	22.1	

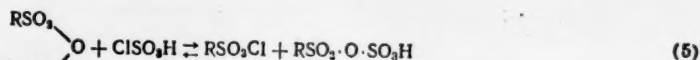
The sodium salts of the sulfonic acids react only very slowly with boiling phosphorus trichloride. Exceptions are the salts of mesitylene- and 2,4,6-triethylbenzenesulfonic acids with a content of about 1 mole of water of crystallization (calculated). In these two cases, exactly as in the case of the free sulfonic acids, anhydrides of the sulfonic acids are formed preferentially (Table 2). In all cases 4 ml  $\text{PCl}_5$  was taken per 0.01 mole of sulfonic acid.

Is it possible to obtain anhydrides of sulfonic acids by reacting sulfonic acids with chlorosulfonic acid.

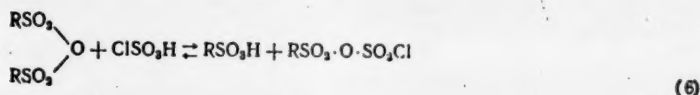
We recently showed [4] that here, just as with acid chlorides of other inorganic acids, the first step is formation of mixed anhydrides  $\text{RSO}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ , due to which the ground is so to speak prepared for further interaction according to the scheme:



The anhydrides actually react further with great facility with chlorosulfonic acid, so that their accumulation (except in the special cases considered below) is impossible. Two courses of this process are conceivable in the initial stage:

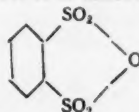


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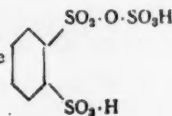
In the first case one half of the quantity of anhydride taken ought to be transformed into sulfochloride immediately after solution of the anhydride in a large excess of  $\text{ClSO}_3\text{H}$ . According to our observations, the sulfonic acids corresponding to the anhydrides react more slowly than the anhydrides with  $\text{ClSO}_3\text{H}$ ; consequently, if scheme (6) is valid, the reaction mixture in the first instant after solution of anhydride should not contain the quantity of sulfochloride corresponding to one half of the anhydride taken. The problem was solved experimentally with the help of the anhydrides of o-dichlorobenzene- and m-nitrobenzenesulfonic acids. As an example we give details of an experiment with the anhydride of m-nitrobenzenesulfonic acid: the finely pulverized substance (0.00125 mole) in a test tube was covered with cooled ( $0^\circ$ ) chlorosulfonic acid (3 ml) while shaking, and poured on to ice after 20-30 seconds to give a nearly transparent solution containing traces of m-nitrobenzenesulfochloride. Consequently only scheme (6) can apply.

The literature describes the formation of the anhydride of benzene-o-disulfonic acid



by reaction of chlorosulfonic acid with the dipotassium salt of the o-disulfonic acid at  $120^\circ$  [5]. It must be assumed that the possibility of obtaining this inner anhydride is governed by its resistance to the action of hot

$\text{ClSO}_3\text{H}$  in association with the great instability of the intermediately formed mixed anhydride



which, undergoes cyclization in the very instant of its formation.

In conclusion we describe a general method of preparation of anhydrides of sulfonic acids by the action of phosphorus pentoxide on sulfonic acids in chloroform, bearing in mind that in a medium of hydrocarbons the formation of the corresponding sulfones is possible [6].

Methods based on interaction of sulfonic acids with acid chlorides of inorganic acids or on sulfonation with oleum (for literature see [7]) do not by any means always lead to anhydrides, and in any case the latter are usually contaminated with sulfochlorides, sulfonic acids and sulfides, which fact complicates their isolation in the pure state. Phosphorus pentoxide was tried out without particular success for the preparation of the

anhydride of o-sulfobenzoic acid [8];  $P_2O_5$  has been used [10] for the preparation of anhydrides of methane- and ethanesulfonic acids and of benzene- and p-toluenesulfonic acids; the yields of the two last anhydrides are low (about 50% of theory), possibly due to overheating of the reaction mixture.

Our procedure was as follows: the sulfonic acid (0.02 mole), containing 1 or two moles of water of crystallization, was suspended in absolute chloroform (15-25 ml) and  $P_2O_5$  powder was gradually added in large excess (6-10 g), the solid being triturated from time to time. Completion of the reaction requires short-period boiling (up to 30 minutes). Completion is marked by the solution becoming perfectly colorless. There are two alternatives for the further working-up: readily soluble anhydrides are taken up in chloroform, the solvent is completely evaporated in vacuum, and the crystalline residue of anhydride is washed with glacial acetic acid and ether. The other case, the reaction mixture is treated with iced water, and the precipitated anhydride is filtered and washed as in the preceding case. Anhydrides of  $\alpha$ - and  $\beta$ -anthraquinonesulfonic acids have a faint yellow color; the remainder are snow white.

TABLE 3

Experiment No.	Aromatic radical of the sulfonic acid	Anhydride		
		yield, % of theory	m.p. deg C	form of crystals (from chloroform or chlorobenzene)
1	$C_6H_5-$	80	90-92	tetrahedral prism
2	$4-ClC_6H_4-$	85.5	appr. 150	tetrahedral prisms of polyhedra
3	$3,4-Cl_2C_6H_3-$	90	118-119	tetragonal tablets or prisms
4	$2,4-Cl_2C_6H_3-$	86	190-195	tetrahedral prisms
5	$4-BrC_6H_4-$	88	170-180	tetrahedral prisms
6	$3,4-Br_2C_6H_3-$	84	163	short prisms
7	$2,4-Br_2C_6H_3-$	89	225-230	tetrahedral prisms
8	$3-(NO_2)C_6H_4-$	80	appr. 160	small tablets
9	$4-CH_3C_6H_4-$	90	125-130	parallelopipeds
10	$3,4-(CH_3)_2C_6H_2-$	85	137-140	tetrahedral prisms
11	$2,4-(CH_3)_2C_6H_2-$	93	153-156	polyhedra
12	$2,5-(CH_3)_2C_6H_2-$	90	126-128	compact tablets or prisms
13	$2,4,6-(CH_3)_3C_6H_0-$	88	appr. 225	tetrahedral prisms
14	$C_{10}H_7-$	84.5	appr. 210	tetrahedral prisms
15	$C_{10}H_7-2$	82	185-190	tetragonal tablets or prisms
16	$C_{10}H_7O_2-1$	56	245-250	indefinite
17	$C_{10}H_7O_2-2$	40	appr. 250	warty

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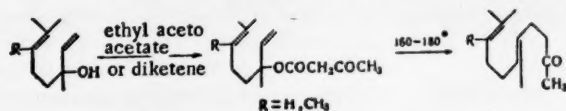
# THE SYNTHESIS OF GERANYLACETONE, 3-METHYLGERANYLACETONE, PSEUDOIONONE AND PSEUDOIRONE

Academician I.N. Nazarov, L. A. Yanovskaya, B.P. Gus'ev,  
S.M. Makin and I.I. Nazarova

In the course of systematic work on the synthesis of isoprenoid compounds [1] our attention was attracted by a short paper by Carrol [2] which reported the formation of geranylacetone in 40-45 % yield on heating linalool with ethyl acetoacetate in presence of a small quantity of sodium ethoxide. This method was also employed later by other authors [3,4] for the preparation of geranylacetone and some of its analogs. An interesting variant of Carrol's synthesis was proposed by Kimel and Cope [5]. By reacting linalool with diketene in presence of metallic sodium, the authors obtained linalyl acetoacetate (61% yield), pyrolysis of which at 170-235° gave geranylacetone (78% yield).

We made a detailed examination of both variants of the synthesis as applied to linalool and 3-methyl-linalool with the objective of development of a method of preparation of geranylacetone and 3-methylgeranylacetone. It was found that the reaction between linalool or 3-methyl-linalool and ethyl acetoacetate proceeds best at a temperature of 160-180° in the absence of any catalysts [6]. Maximum yields (65-70%) of geranylacetone and 3-methylgeranylacetone were attained by using a twofold excess of ethyl acetoacetate and by carrying out the reaction with the utmost speed. Up to 90-95% of the theoretical amount of carbon dioxide was evolved (the content of CO<sub>2</sub> analyzed over 99%) during the reaction, and nearly the theoretical amount of alcohol, containing a trace of acetone, was distilled off.

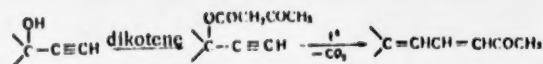
It should be noted that distillation of the alcohol is completed very much sooner than the evolution of carbon dioxide. The formation of geranylacetone and 3-methylgeranylacetone would therefore appear to proceed via the acetoacetate stage according to the scheme:



We confirmed this mechanism [1] in the reaction between dimethylvinylcarbinol and ethyl acetoacetate when we succeeded in isolating the acetoacetate of dimethylvinyl carbinol, the pyrolysis of which gives methylheptenone.

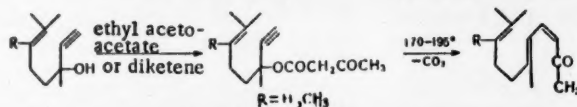
In a study of the second variant of the synthesis we established that acylation of linalool and 3-methyl-linalool by diketene proceeds best in presence of pyridine or triethylamine, and not in presence of metallic sodium. Under our conditions the yield of the corresponding acetoacetates is 85-90%. Pyrolysis of the latter is best performed at maximum speed at a temperature of 160-200°. Both steps (acylation and pyrolysis) can be performed without isolation and purification of the intermediate acetoacetate.

On the basis of the data obtained, we decided to investigate both variants of the process, starting from dehydrolinalool and 3-methyldehydrolinalool, with the aim of developing methods of synthesis of pseudoionone and pseudoirone. The start of this work coincided with the publication by Lacey [7] of a paper demonstrating the possibility of synthesis of dienones according to the general scheme:



The starting substances in Lacey's work were dimethylethynyl carbinol and some of its simplest derivatives. Lacey carried out the second step of the reaction (pyrolysis of the acetoacetate) in presence of a small quantity of *p*-toluenesulfonic acid. We made a detailed study of this route to dienones in our laboratory starting from a whole series of tertiary acetylenic alcohols [8]. While our work was in the press a short note appeared by Naves [9] that drew attention to the possibility of employing the reaction between dehydrolinalool or 3-methyldehydrolinalool and ethyl acetoacetate or diketene for synthesis of pseudoionone and pseudoirone. Naves later [10] gave full details of the preparation of 3-methylpseudoirone from 3-methyldehydrolinalool and  $\alpha$ -methylacetoacetic ester. Finally, N. A. Preobrazhensky et al. [11] recently announced the preparation of pseudolionone from dehydrolinalool and diketene via the acetoacetate of dehydrolinalool.

We studied both of these variants of the synthesis and established that the reaction between dehydrolinalool or 3-methyldehydrolinalool and ethyl acetoacetate proceeds best by heating in a nitrogen atmosphere at 170-180° in the absence of catalysts. Under these conditions the yield of pseudoionone and pseudoirone is about 55%.



Acylation of dehydrolinalool or 3-methyldehydrolinalool proceeds best of all in presence of pyridine or triethylamine at 70-80°. Pyrolysis of the resultant acetoacetates of dehydrolinalool and 3-methyldehydrolinalool was conducted at 185-195°. Approximately 80-85% of the theoretical amount of carbon dioxide (the CO<sub>2</sub> content analyzed at over 90%) is evolved during pyrolysis. The yield of pseudoionone and pseudoirone, calculated on the original dehydrolinalool or 3-methyldehydrolinalool, is 50-55%.

Cyclization of the resultant pseudoionone with the help of a mixture of sulfuric and glacial acetic acids [12] gave ionone in a yield of 65%.

## EXPERIMENTAL

**1. Preparation of geranylacetone.** a) A mixture of 77 g (0.5 mole) linalool and 130 g (1 mole) ethyl acetoacetate was quickly heated to 160-180° (after the air had been purged out with nitrogen) and held at this temperature until gas ceased to come off (about 3-4 hours). About 10 liters of carbon dioxide (88% of theory) was evolved, and 25.8 g of alcohol (b.p. 75-78°) was distilled off. Two fractionations of the residue gave 70 g (about 70%) of geranylacetone with b.p. 92-94°/3 mm,  $n_D^{20}$  1.4674;  $\lambda_{\text{max}}$  (in methanol) 291 m $\mu$  (log  $\epsilon$  = 2.42).

Found %: C 80.55; 80.49; H 11.37; 11.42 C<sub>15</sub>H<sub>22</sub>O. Calculated %: C 80.35; H, 11.41

Semicarbazone: m.p. 95-96° (from alcohol).

Found %: N 16.42; 16.42 C<sub>14</sub>H<sub>25</sub>O<sub>3</sub>. Calculated %: N 16.71

b) To a mixture of 15.4 g (0.1 mole) linalool and 0.6 g pyridine was added (in the course of 15 minutes) 10 g (0.11 mole) of diketene, after which the mixture was stirred for 2 hours at room temperature and 2 hours at 60-65°. The product was washed with bicarbonate solution and with water and dried with magnesium sulfate. Fractional distillation gave 20.4 g (85% of theory) of linalyl acetoacetate with b.p. 132-134° at 2 mm;  $n_D^{20}$  1.4706.

18.8 g of the linalyl acetoacetate was heated at 165-200° for 30 minutes. 920 ml of carbon dioxide came off. Two fractional distillations gave 10.8 g (70% of theory) of geranylacetone with b.p. 88-89°/1 mm;  $n_D^{20}$  1.4664. The semicarbazone melted at 94-94.5° and did not give a depression in admixture with the previously prepared specimen.

**2. Preparation of 3-methylgeranylacetone (I, R = C<sub>11</sub>H<sub>23</sub>).** a) Reaction between 20 g of 3-methylallinool and 35 g of ethyl acetoacetate by the above procedure (experiment 1 a) gave 18 g of 3-methylgeranylacetone with b.p. 105-107° at 2 mm;  $n_D^{20}$  1.4702.

Found %: C 79.48; 79.54; H 11.59; 11.54 C<sub>14</sub>H<sub>24</sub>O. Calculated %: C 80.71; H 11.67

The semicarbazones melted at 101-102° and 138-139°.

b) Reaction of 19 g of 3-methylallinool and 13 g of diketene in presence of 0.5 ml pyridine at 70° gave the acetoacetate which was pyrolyzed at 160-190° as described in experiment 1 b. Two fractional distillations gave 11.5 g of 3-methylgeranylacetone with b.p. 106-108°/2 mm;  $n_D^{20}$  1.4697.

**3. Preparation of pseudoionone.** a) Reaction between 152 g of dehydrolinalool and 260 g of ethyl acetoacetate was conducted at 170-180° for 4½ hours as described under experiment 1 a. After distillation of the volatile components (up to 100°/10 mm), the residue was boiled and stirred with three times the volume of 25% sodium bisulfite for 5 hours. The mixture was washed twice with ether and the bisulfite derivative of pseudoionone was decomposed with 10% sodium hydroxide solution in presence of ether by the usual method. Fractional distillation of the ether extract gave 106 g (55 % of theory) of pseudoionone with b.p. 123-125° at 4 mm;  $n_D^{20}$  1.5310;  $\lambda_{\max}$  (in isooctane) 280 mμ (log ε = 4.36); 2,4-dinitrophenylhydrozone: m.p. 146-146.5° (from alcohol).

Found %: N 15.12; 14.97 C<sub>14</sub>H<sub>22</sub>ON<sub>2</sub>. Calculated %: N 15.05

b) A mixture of 15.2 g of dehydrolinalool and 10 g of diketene was heated in presence of triethylamine at 75-80° for 3 hours. The product was dissolved in ether, washed with 5% bicarbonate solution and dried with magnesium sulfate. Fractional distillation gave 21.2 g (90% of theory) of the acetoacetate of dehydrolinalool with b.p. 95-96° at 0.07 mm;  $n_D^{20}$  1.4685;  $d_4^{20}$  0.9879.

Found %: C 71.40; 71.60; H 8.60; 8.52 C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>. Calculated %: C 71.14; H 8.53

Pyrolysis of 11.8 g of the acetoacetate of dehydrolinalool was carried out at 185-195° for 25 minutes. Fractional distillation gave 4.8 g (50% of theory) of pseudoionone with b.p. 89-90° at 0.1 mm;  $n_D^{20}$  1.5285;  $\lambda_{\max}$  (in isooctane) 281 mμ (log ε = 4.38).

Found %: C 80.97; 80.99; H 10.30; 10.43 C<sub>13</sub>H<sub>20</sub>O. Calculated %: C 81.19; H 10.49

The 2,4-dinitrophenylhydrozone was obtained in the form of two isomers with m.p. 147-148° (93%) and m. p. 117-118° (7%).

Pseudoionone obtained from natural citral had  $\lambda_{\max}$  (in isooctane) 282 mμ (log ε = 4.37).

**Cyclization of pseudoionone [13].** 96 g of pseudoionone was added dropwise in 35 minutes at 5-15° to a mixture of 240 g of glacial acetic acid and 400 g of sulfuric acid (d 1.84). The mixture was stirred for 30 minutes at 28-30°, poured on to ice and extracted with toluene. The organic layer was washed with saturated bicarbonate solution, the solvent was distilled off in low vacuum, and the residue was distilled with steam at 30-35 mm until the oil had come over completely. The distillate was extracted with ether, and the ether layer (dried with magnesium sulfate) was fractionated to give 63 g (65% of theory) of ionone with b.p. 94-97° at 1 mm;  $n_D^{20}$  1.5190 (content of β-form 97%).

Found %: C 81.07; 80.88; H 10.23; 10.44 C<sub>13</sub>H<sub>20</sub>O. Calculated %: C 81.19; H 10.49

The semicarbazone of β-ionone was obtained with m.p. 148-149° (from aqueous methanol).

**4. Preparation of pseudofrone.** a) Heating of a mixture of 25 g of 3-methyldehydrolinalool and 40 g of ethyl acetoacetate at 180-190° for 4 hours gave a mixture of isomeric pseudofrones. Two fractional distillations gave 15.8 g (51% of theory) of pseudofrone with b.p. 118-129° at 1 mm;  $n_D^{20}$  1.5140-1.5284;  $d_4^{20}$  0.9117-0.9097.

For the fraction with b.p. 118-120° at 1 mm:

Found %: C 81.08; 80.95; H 10.62; 10.58

For the fraction with b.p. 124-129° at 1 mm:

Found %: C 81.03; 80.75; H 10.73; 10.63 C<sub>14</sub>H<sub>22</sub>O. Calculated %: C 81.49; H 10.74

The 2,4-dinitrophenylhydrozone was separated into isomers by crystallization from alcohol and a mixture of alcohol and ethyl acetate; m.p. 153-154° and 120-121°.

b) Reaction of 20 g of 3-methyldehydrolinolol with 12 g diketene in presence of 0.5 ml pyridine at 70° gave the acetoacetate which was washed with saturated sodium bicarbonate solution, extracted with ether and dried with magnesium sulfate. The ether was driven off and the residue (without distillation) was subjected to pyrolysis by the usual method at 180-200° for 40 minutes. After fractional distillation, 13.1 g (53% of theory) of a mixture of isomeric pseudofrones was obtained; b.p. 102-115° at 1 mm;  $n_D^{20}$  1.5192-1.5280.

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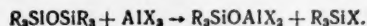
# NEW HALOGEN-CONTAINING ORGANOALUMINUM-SILICON COMPOUNDS OF THE TYPE OF $R_3SiOAlX_2$

N. F. Orlov

(Presented by Academician L. N. Nazarov, March 12, 1957)

Compounds of the type  $R_3SiOAlX_2$  (where  $X = Cl, Br$ ) have not been described in the literature. A paper by M. B. Voronkov, B.N. Dolgov and A.N. Dmitrieva [1] refers to the possibility of formation of compounds of this type, but they did not isolate them. A short communication by Simmler [2] mentions the separation of  $(CH_3)_3SiOAlCl_2$  by reaction of trimethylethoxysilane with aluminum chloride, but the author does not give the constants of the compounds nor the analytical data, and he indicates that his compound does not distill in vacuum.

We have developed a method of synthesis of compounds of the above type by heating equimolar quantities of hexaalkyldisiloxane with aluminum halide while distilling off the corresponding trialkylhalosilane. Heating of the reaction mixture is stopped when its temperature is approximately 20-30° higher than the boiling point of the original hexaalkyldisiloxane. Reaction is effected to give a yield of 70-85% according to the equation:



The trialkylsiloxy-aluminum dihalides are colorless, crystalline substances that distill in vacuum, are stable in dry air and react violently with water. They are readily soluble in ether, benzene, carbon tetrachloride and hexane.

In contrast to the hexaalkyldisiloxanes, hexachlorodisiloxane does not react with aluminum chloride under analogous conditions.

## EXPERIMENTAL

The starting hexaalkyldisiloxanes, distilled over sodium, had the constants listed in Table 1.  $AlBr_3$  was "pure for analysis",  $AlCl_3$  was sublimed in vacuum. All experiments were carried out in the absence of atmospheric moisture in a distillation flask attached to a 10 cm Vigreux column which was connected to a Liebig condenser and a receiver. Two thermometers (one in the flask and one in the column) enabled the temperature of the reaction mixture in the flask and that of the evolved trialkylhalosilane vapor to be checked. The latter compounds were redistilled, after which they had the constants given in Table 2.

The trialkylsiloxy-aluminum dihalides were isolated either by recrystallization from hexane or by fractional distillation in vacuum.

The melting point was determined in sealed capillaries.

Halogen was determined in weighed samples by Volhard titration of an aqueous dioxane solution of the substance. Silicon was determined by wet combustion of the substance with a mixture of oleum and nitric acid.

Following calcination at 1000°, the  $SiO_2$  was treated, as a further precaution, with a mixture of sulfuric and hydrofluoric acids. Aluminum was determined in the filtrate, after separation of the silica, by precipitation with ammonia in presence of methyl red. The precipitate of aluminum hydroxide was calcined to  $Al_2O_3$  at 1200°.



TABLE 1

Properties of Hexaalkyldisiloxanes

Compound	b.p., deg C	Pressure mm mer- cury	$d_4^{20}$	$n_D^{20}$	MR <sub>D</sub>	
					found	calc.
(CH <sub>3</sub> ) <sub>6</sub> Si <sub>2</sub> O	100.5	765	0.7625	1.3765	48.92	48.89
(CH <sub>3</sub> ) <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Si <sub>2</sub> O	150.5	750	0.7969	1.4012	48.18	58.09
(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Si <sub>2</sub> O	192	760	0.8199	1.4179	67.44	67.13
(C <sub>2</sub> H <sub>5</sub> ) <sub>6</sub> Si <sub>2</sub> O	231	760	0.8443	1.4330	76.70	75.87

TABLE 2

Properties of Trialkylhalosilanes

Compound	b.p., deg C	Pressure mm mer- cury	$d_4^{20}$	$n_D^{20}$	MR <sub>D</sub>	
					found	calc.
(CH <sub>3</sub> ) <sub>3</sub> SiCl	58	760	0.8549	1.3870	29.91	29.93
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> SiCl	90.5	745	0.8756	1.4050	34.54	34.34
CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiCl	119.5	732	0.882	1.4180	39.17	39.05
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	145.5	753	0.8963	1.4300	43.80	43.44
(CH <sub>3</sub> ) <sub>3</sub> SiBr	80	768	1.1725	1.422	32.91	33.18
C <sub>2</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> SiBr	111	750	1.1548	1.4345	37.54	37.72
CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiBr	138	760	1.1426	1.4460	42.17	42.27
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiBr	163	760	—	1.4570	—	—

**Synthesis of CH<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SiOAlCl<sub>2</sub>.** A mixture of 43.6 g (0.2 mole) of tetraethyldimethyldisiloxane and 26.6 g (0.2 mole) aluminum chloride was gradually heated. Methyl-diethylchlorosilane started to distil over at a flask temperature of 135°. Heating was continued for 1 hour and was stopped when the temperature in the flask had reached 210° and the temperature of the vapor was 122°. A total of 24 g of CH<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SiCl (87.5% of theory) was isolated; b.p. 116-122°. The residue in the flask was distilled in vacuum and gave 36 g of methyl-diethylsiloxy-aluminum dichloride with b.p. 143-147° at 4 mm (83.5% of theory).

The constants listed in Table 3 were obtained after a second vacuum distillation.

**Synthesis of (CH<sub>3</sub>)<sub>3</sub>SiOAlBr<sub>2</sub>.** 80 g (0.3 mole) of AlBr<sub>3</sub> was charged into a distilling flask containing 65 g (0.4 mole) of hexamethyldisiloxane. After one minute the flask contents generated heat and boiled up; at the same time the AlBr<sub>3</sub> dissolved. The reaction mixture was heated and trimethylbromosilane started to distil over. Heating was stopped when the flask temperature was 115°. 36 g (67%) of (CH<sub>3</sub>)<sub>3</sub>SiBr with b.p. 79-81° was collected; also 6 g of a mixture of trimethylbromosilane and hexamethyldisiloxane with b.p. 81-92°. The entire contents of the flask crystallized on cooling to room temperature. Trimethylsiloxy-aluminum dibromide had the constants given in Table 3 after two recrystallizations from hexane.

The yield of crude product was about 70%.

**Reaction of AlCl<sub>3</sub> with hexachlorodisiloxane.** A mixture of 28.5 g (0.1 mole) hexachlorodisiloxane (b.p. 134° at 760 mm) and 13.3 g (0.1 mole) AlCl<sub>3</sub> was heated to the boil for 5 hours, the temperature of the mixture remaining constant for the whole time at 133-134°. Distillation gave only unchanged hexachlorodisiloxane.

**Hydrolysis of (CH<sub>3</sub>)<sub>3</sub>SiOAlCl<sub>2</sub>.** In the course of 30 minutes 9.35 g (0.05 mole) of (CH<sub>3</sub>)<sub>3</sub>SiOAlCl<sub>2</sub> was added with shaking to a separating funnel containing 50 ml water. The organic layer, weighing 3.3 g (81.5%),



TABLE 3

Trialkylsiloxy-aluminum Dihalides

Compound	b.p. deg C	Pressure, mm mercury	M.p., deg C	Si, %		Al, %		Halogen, %	
				calc.	found	calc.	found	calc.	found
$(\text{CH}_3)_2\text{SiOAlCl}_2$	102	4	88	15.01	14.75; 14.64	14.42	14.58; 14.74	37.90	37.97; 37.99
$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiOAlCl}_2$	125	4	46.5	13.97	13.50; 13.26	13.41	13.70; 13.79	35.26	35.00; 35.00
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiOAlCl}_2$	143	4	33*	13.06	12.95; 12.93	12.54	12.52; 12.52	32.96	32.81; 33.25
$(\text{CH}_3)_2\text{SiOAlCl}_2$	173	4	43*	12.26	12.28; 12.33	11.77	11.74; 11.81	30.94	30.89; 31.02
$(\text{CH}_3)_2\text{SiOAlBr}_2$	127	4	111.5-113	10.17	9.96; 9.97	9.77	9.46; 9.70	57.91	57.6; 57.3
$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{SiOAlBr}_2$	150	2.5	66	9.67	9.67; 9.43	9.30	9.20; 9.43	55.11	55.45; 55.00
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiOAlBr}_2$	173	3.5	55	9.24	9.22; 8.80	8.87	8.75; 8.77	52.57	52.52; 52.17
$(\text{C}_2\text{H}_5)_2\text{SiOAlBr}_2$	181	3	73*	8.83	8.56; 8.25	8.48	8.44; 8.04	50.25	50.12; 49.56

\* M.p. of the twice-distilled substances (without recrystallization).

was separated and dried over potassium carbonate. After distillation the hexamethyldisiloxane had b.p. 100.0°,  $d_4^{20}$  0.7647,  $n_D^{20}$  1.3768. Literature data [3]: b.p. 100.4°,  $d_4^{20}$  0.7637,  $n_D^{20}$  1.3774.

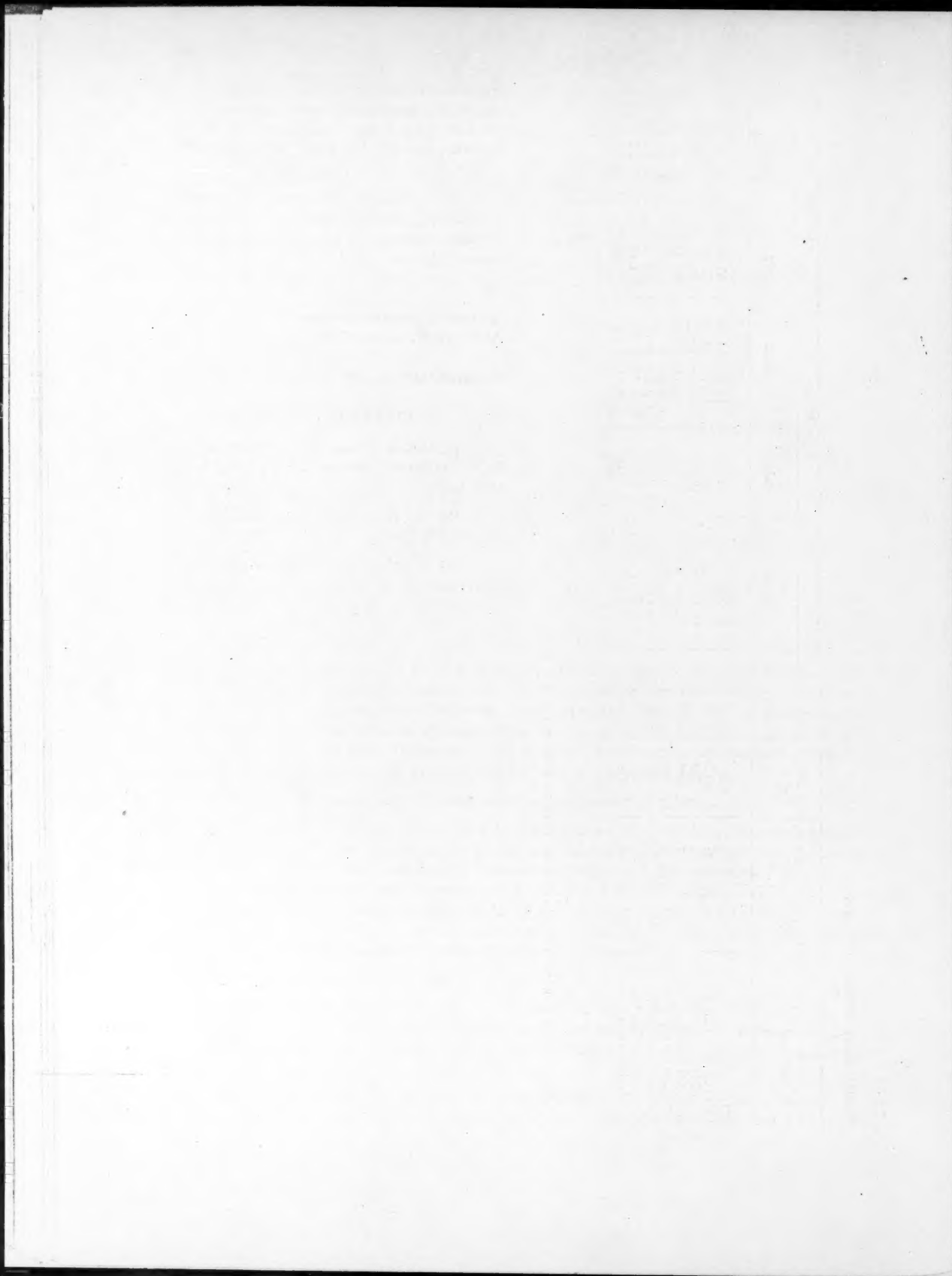
The author takes this opportunity of expressing his deep gratitude to Professor B.N. Dolgov for his guidance and to M. G. Voronkov for his valuable advice.

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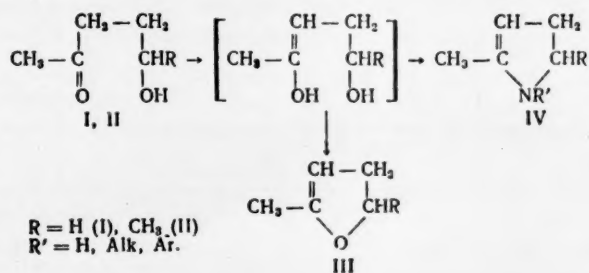
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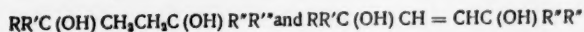
# THE SYNTHESIS OF PYRROLES, PYRROLINES AND PYRROLIDINES FROM $\gamma$ -KETOALCOHOLS

Corresponding Member of the Academy of Sciences A.P. Terentyev,  
M.A. Volodina, N.L. Podlesova and N.E. Golubeva

We showed earlier [1] that the hydroamination of  $\gamma$ -ketoalcohols with formamide or its N-substituted derivatives leads to formation of nitrogen-containing heterocycles. The products of the reaction were pyrrolidine bases. The process of formation of a five-membered nitrogen-containing heterocycle from  $\gamma$ -ketoalcohols (I, II) can also be interpreted as the cleavage of water from the molecule of the alcohol and ammonia (or amine) over a dehydration catalyst. The product of such a transformation must be the corresponding  $\Delta^3$ -pyrroline (IV).

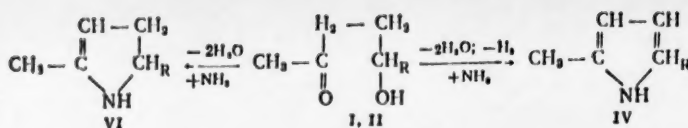


It is entirely possible that one of the products of the reaction is a homolog of 4,5-dihydrofuran (III). The probability of such a type of transformation is supported by data in the literature on catalytic dehydration of 1,4-diols of the type of



and their joint catalytic dehydration with ammonia and alkyl- and arylamines [2-4]. Yu. K. Yuryev and L.K. Korobitsyna [4] showed that joint catalytic dehydration of cis-buten-2-diol-1,4 leads to formation of the  $\Delta^3$ -pyrroline ring only when aniline is employed. On reacting cis-buten-2-diol-1,4 with ammonia they detected only traces of pyrrole and found no  $\Delta^3$ -pyrroline at all.

Our objective was to study the behavior of  $\gamma$ -ketoalcohols towards dehydration catalysts in order to find new routes to the relatively little studied and difficultly accessible  $\Delta^3$ -pyrrolines, as well as to the products of their dehydrogenation - pyrroles.



A method of this type for the synthesis of  $\Delta^2$ -pyrrolines has not previously appeared in the literature, nor has any work been published on their behavior over dehydration and dehydrogenation catalysts.

Compounds used in the present investigation were  $\gamma$ -acetopropyl alcohol (I) and secondary  $\gamma$ -acetobutyl alcohol (II).

It was found that the transformation of  $\gamma$ -acetopropyl alcohol in a stream of ammonia at 450° over alumina and Pd on asbestos (similarly over Ni/Al<sub>2</sub>O<sub>3</sub>) leads to formation of  $\alpha$ -methylpyrroline (V),  $\alpha$ -methylpyrrole (VI) in 10-20% yield and a small quantity of  $\alpha$ -methyl- $\Delta^2$ -pyrroline (IV).

Apparently the primary product of the reaction is  $\Delta^2$ -pyrroline; the latter undergoes disproportionation under the catalytic conditions (on the lines of Zelinsky's irreversible catalysis [5]) to give V and VI.

Formation of  $\alpha$ -methylpyrrole can result from dehydrogenation of  $\alpha$ -methyl- $\Delta^2$ -pyrroline both under the influence of Pd and of the alumina itself. The latter effect was observed by Yu. K. Yuryev and I.K. Korobitsyna in the catalytic transformation of cis-buten-2-diol-1,4 with aniline [4].

A study of the reaction over alumina without Ni and Pd showed that the main product of the reaction is  $\alpha$ -methyl- $\Delta^2$ -pyrroline (45 %); under these conditions very little  $\alpha$ -methylpyrrole is formed. In our case, therefore, alumina has substantially no influence upon the dehydrogenation of IV.

Reaction of ketoalcohols (I and II) with ammonia over alumina with metals and without metals (Ni, Pd) at 450° leads to formation of a large amount of high-boiling resinous substances. In order to avoid this, we tried the "milder" catalyst described for processes of dehydrocyclization of anils - chromium oxide/copper-on-carbon [6].

It was shown that a temperature of 600° and higher was too high for our starting substance and led to considerable resinification and cracking. At lower temperatures (480-500°)  $\gamma$ -acetopropyl alcohol (I) in a stream of ammonia gave  $\gamma$ -methyl- $\Delta^2$ -pyrroline (IV) as the main product (25%) and only traces of  $\alpha$ -methyl- $\Delta^2$ -pyrroline (IV).

When using the copper-chromium catalyst, the process of amination of I is accompanied by formation of a considerable quantity of 2-methyl-4,5-dihydrofuran (III).

We also observed these transformations under similar conditions when starting from secondary  $\gamma$ -acetobutyl alcohol.

Consequently, the most favorable conditions for formation of  $\alpha$ -methyl- $\Delta^2$ -pyrroline from  $\gamma$ -acetopropyl alcohol were the use of  $\gamma$ -alumina as catalyst at a temperature of 310-320°.

Having established satisfactory conditions of synthesis of  $\alpha$ -methyl- $\Delta^2$ -pyrroline, we decided to employ  $\gamma$ -ketoalcohols (I and II) for the synthesis of a series of little studied and interesting  $\Delta^2$ -pyrroline bases.

Some homologs of  $\Delta^2$ -pyrroline are known to have practical value as photosensitizers [7].

We succeeded in showing that on passing the ketoalcohols (I and II) in a stream of ammonia or amine or in admixture with an aromatic amine over alumina at 310-320°,  $\Delta^2$ -pyrroline bases are formed in a yield of 25-55%. At lower reaction temperatures (280-290°) the pyrroline bases contain a considerable quantity of the corresponding 4,5-dihydrofurans (III).

A study of the mechanism of the reaction was not the immediate purpose of our investigation and will be the subject of a later study. In all probability, a more detailed examination of the reaction conditions (use of other dehydration catalysts [3], activation of the alumina [2-4]) would enable the yield of pyrroline bases to be increased slightly.

Preliminary examination of the properties of some of the  $\Delta^2$ -pyrrolines prepared in this manner showed that they readily form compounds with alkyl halides, add on bromine when treated with dioxane dibromide, react with Grignard reagents and (in some cases) react with phenylisothiocyanate, etc.

The position of the double bond in the prepared pyrrolines cannot yet be said to be established with certainty, but they are most probably  $\Delta^2$ -pyrrolines. This is supported by a study of some of the properties of the prepared pyrrolines and by their identity with substances whose structure is beyond doubt.

Preliminary tests with some of the prepared  $\Delta^2$ -pyrrolines at the Institute of Pharmacology of the Academy of Medical Sciences of the USSR (laboratory of Prof. Andreev) showed that they possess considerable physiological activity.

#### EXPERIMENTAL \*

Use was made in the investigation of commercial acetopropyl alcohol; after distillation in vacuum, this had b.p. 114-115°/30 mm;  $n_D^{20}$  1.4395,  $d_4^{20}$  1.0068 [8].

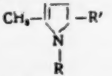
Secondary  $\gamma$ -acetobutyl alcohol was obtained by condensation of sodium ethyl acetoacetate with propylene oxide [9]: b.p. 60-61°/4 mm;  $n_D^{20}$  1.4328;  $d_4^{20}$  0.9634. The following catalysts were used: commercial  $Al_2O_3$ , Pd on asbestos; Ni/ $Al_2O_3$ ,  $Cr_2O_3$ /Cu on carbon. Conditions of catalysis were: diameter of tube 13 mm, length of catalyst bed 40 cm (in the case of  $Al_2O_3$  and Pd it was 35 cm  $Al_2O_3$  and 20 cm Pd on asbestos), rate of passage of ketoalcohol 0.5 ml/min; the ammonia was taken from a cylinder, or a 1:2 mixture of ketoalcohol and amine was passed through.

Results of the experiments are presented in Table 1 and 2.

TABLE 1

Starting substances	Catalyst	Temperature, deg C	Analysis of picrate, % N			
			III	IV	V	VI
$\gamma$ -Acetopropyl alcohol (I)	Ammonia	$Al_2O_3$ + Pd	450	—	5	10
		$Al_2O_3$	330-350	—	35	3
		$Cr_2O_3$ /Cu/C	480-500	20	20	4
$\gamma$ -Acetobutyl alcohol (II)	Ammonia	$Al_2O_3$	330-350	—	30	5
		$Cr_2O_3$ /Cu/C	480-500	18	22	3
						4

TABLE 2

Starting substances		R and R' of the pyrroline base 	M.p. of of picrate deg C	Analysis of picrate, % N	
				found	calc.
$CH_3CO(CH_2)_2CH_2OH$	$NH_3$	R=H <sup>(*)</sup> R'=H	120-120.5	18.01 17.82	17.95
The same	$CH_3NH_2$	R=CH <sub>3</sub> <sup>(10)</sup> R'=H	216-218	17.17 17.01	17.17
" "	$C_6H_5NH_2$	R=C <sub>6</sub> H <sub>5</sub> <sup>(11)</sup> R'=H	103-105	14.22 14.44	14.45
" "	$n-C_8H_{17}NH_2$	R=n-C <sub>8</sub> H <sub>17</sub> <sup>(11)*</sup> R'=H	124-126	14.15 13.89	13.93
$CH_3CO(CH_2)_2CHOHCH_3$	$NH_3$	R=H <sup>(12)</sup> R'=CH <sub>3</sub>	131-132	17.25 17.38	17.17

\* V. V. Dorokhova and B. S. Kikot participated in some of the syntheses.

\*\* The melting point of the picrate of N-p-tolyl-2-methyl- $\Delta^2$ -pyrroline deviates from the literature data, but the analysis of the picrate and the  $M_{RD}$  of the base leave no doubt about the purity of the prepared N-p-tolyl-2-methyl- $\Delta^2$ -pyrroline.

Table 1 gives the results of experiments on joint catalytic dehydration of  $\gamma$ -acetopropyl alcohol and secondary  $\gamma$ -acetobutyl alcohol with ammonia over alumina with Pd, alumina without Pd and chromium / copper catalyst.

The constants of the compounds prepared by this method were close to the literature data. The pyrrolidines and  $\Delta^2$ -pyrrolines were characterized as the picrates.

Table 2 contains the results of transformations of ketoalcohols (I and II) with ammonia and amines over alumina. The prepared  $\Delta^2$ -pyrrolines were characterized as the picrates. All the picrates were analyzed. The constants of the  $\Delta^2$ -pyrrolines agree with the literature data.

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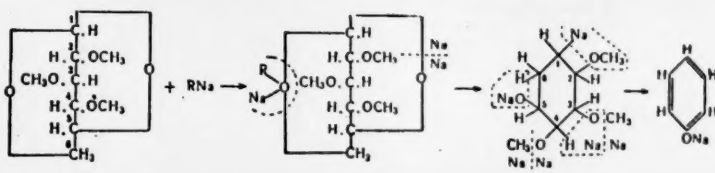


# THE TRANSFORMATION OF LEVOGLUCOSAN INTO AROMATIC COMPOUNDS

N. N. Shorygina and G.V. Perfilova

(Presented by Academician B. A. Kazansky, January 12, 1957).

Micheel [1] was the first to achieve the transition from carbohydrates to carbocyclic compounds; he obtained dimethylene tetrahydroxycyclohexane by heating 1,6-dilodomethylene mannitol with silver at 165-170° for 8 hours. The first successful attempt at transformation of carbohydrates into aromatic compounds was made by P.P. Shorygin and N.N. Shorygina [2]; by the action of metallic sodium in liquid ammonia on trimethyl levoglucosan they obtained phenol in a yield of 34%. The authors put forward a scheme for this transformation based on the rupture of the ethereal bonds by metallic sodium.



The present communication is a continuation of the above investigation whose purpose is a more detailed study of this interesting reaction.

Levoglucosan was obtained by dry distillation of starch in vacuum (yield 14%); its trimethyl ether was obtained by methylation with dimethyl sulfate. An experiment carried out under the conditions described in [2] gave the same result (phenol was obtained in 31% yield.)

Some changes in the experimental procedure and in the method of isolation of the products enabled phenol to be obtained in a yield of 50-56% of theory (according to the above scheme).

Experiments were carried out in the following manner: into a 300 ml ampoule was charged a weighed amount of trimethyl levoglucosan which was dissolved in dry liquid ammonia; to the solution was then gradually added metallic sodium in 30 minutes. The ampoule was left in a Dewar vessel containing dry ice overnight (18 hours); on the following day the ampoule was sealed and left at room temperature. Completion of the reaction was marked by complete decolorization of the dark blue solution of sodium in ammonia. Prior to opening, the ampoule was cooled, the ammonia was removed, and the contents were washed first with moist ether and then with water acidified with  $H_2SO_4$ . The ether extract from the acidic (to congo) aqueous solution was dried with anhydrous sodium sulfate. After the ether had been driven off, a dark brown syrup was left from which the phenol was distilled with steam. The phenol in the distillate was determined by Koppeschaar's method. The ethereal extract of the aqueous distillate was dried and the ether was driven off to leave pure phenol; the latter crystallized on cooling and gave the characteristic benzoate with m.p. 68-69° by the Schotten-Baumann reaction.

Results of experiments (see Table 1) showed that phenol is the main product of the reaction.

TABLE 1

Preparation No.	Taken in the reaction			Duration of reaction (days)	Yield of phenol (%)	Notes
	trimethyl levoglucosan (moles)	sodium (moles per mole of trimethyl levoglucosan)	liquid ammonia (ml)			
1	0.005	6	15	16	50	Mechanical shaking of ampoule ditto
2	0.019	6	45	16	50	
3	0.02	6	50	16	54	
4	0.01	6	25	3	51	
5	0.005	6	15	3	55	

Periodic shaking of the reaction mixture after sealing of the ampoule, as was to be expected, speeded up the reaction nearly 5-fold (see Table 1, exp. 4, 5). It was also considered of interest to establish the influence of the quantity of sodium on the yield of phenol. Formation of bright red products of interaction of trimethyl levoglucosan with metallic sodium, which disappear in course of time, indicates that organosodium compounds may be intermediates in this reaction.

As we see from the data in Table 2, the yield of phenol is directly proportional to the quantity of sodium up to a maximum which corresponds to 6 atoms per mole of trimethyl levoglucosan, as are necessary for cleavage of three ether groups.

TABLE 2

Preparation No.	Taken in reaction			Duration of cooling of ampoule (hours)	Yield of phenol, %
	Yield of phenol (%)	sodium (moles per mole of trimethyl levoglucosan)	liquid ammonia (ml)		
1	0.01	3	25	3	24.5
2	0.01	4.5	25	4	41.8
3	0.01	6	25	4	51
4	0.01	9	25	8	52

In experiments with a smaller amount of sodium, unreacted trimethyl levoglucosan was recovered; excess of sodium does not increase the yield of phenol.

This fact has great importance, for it indirectly confirms the scheme for the reaction proposed by P. P. Shorygin and N.N. Shorygina.

As was further shown by the experiments presented in Table 3, the temperature influences the reaction course. Formation of phenol depends upon the period for which the reaction mixture is held at the temperature of dry ice. The shorter this period the more rapid was the reaction, but the yield of phenol then dropped. The minimum period of cooling necessary for obtaining the maximum yield of phenol was established. In addition to phenol itself, the formation of the dihydric phenols pyrocatechol and resorcinol was also detected.

An ethereal extract was taken from the aqueous solution after distillation of the phenol. After drying and removal of the ether, a dark syrup remained which was chromatographed. Chromatograms were obtained on "wab" paper by the descending method, using a mixture of benzene, ligroine and water (1:1:1) as the solvent; diazotized sulfanilamide served as developer.

TABLE 3

Preparation No.	Taken in reaction			Duration of cooling of ampoule (hours)	Period for decolorization of reaction mixture at room temp (hrs).	Yield of phenol (%)
	trimethyl levoglucosan (moles)	sodium (moles per mole of trimethyl levoglucosan)	liquid ammonia (ml)			
1	0.005	6	15	2	3	40.6
2	0.005	6	15	5	3	44
3	0.005	6	15	8	50	48
4	0.005	6	15	10	50	55
5	0.005	6	15	19	50	53
6	0.005	6	15	25	50	51

Work on the investigation of the carbocyclization of 1,6-anhydrides of hexoses is continuing.

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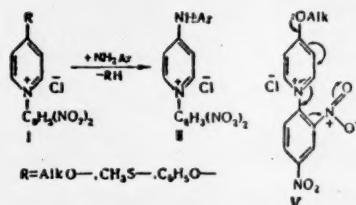


# NEW TRANSFORMATIONS OF PYRIDINIUM SALTS AND THE SYNTHESIS OF $\gamma$ -AMINO SUBSTITUTED PYRIDINES

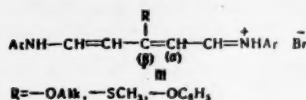
A. F. Vompe, N. V. Monich, N. F. Turitsyna and L. V. Ivanova

(Presented by Academician A. N. Nesmeyanov, June 19, 1957)

Earlier we had attempted to open the pyridine ring in  $\gamma$ -alkoxy, phenoxy and methylmercapto substituted pyridines by treating the chloro-(2,4-dinitrophenylates) of pyridine bases (I) with aromatic amines [1]. Here it was found that the pyridine ring is not cleaved, and instead there occurs substitution of the alkoxy (methylmercapto, phenoxy) group on the aromatic amine radical, with the formation of the chloro-2,4-dinitrophenylates of  $\gamma$ -arylaminopyridines (II) [1]:



Later we were able to accomplish the rupture of the pyridine ring in  $\gamma$ -alkoxy (methylmercapto, phenoxy) pyridines by treating these compounds with cyanogen bromide and aromatic amines [2]. Here we obtained the  $\beta$ -alkoxy (methylmercapto, phenoxy) substituted glutamic aldehydes as the dianil salts (III).



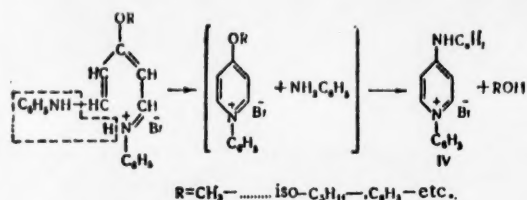
Of these compounds the  $\beta$ -alkoxy substituted derivatives (III;  $R = \text{AlkO}-$ ) are characterized by a great lack of stability even in the crystalline state. • Their alcohol solutions are especially unstable, rapidly undergoing decolorization when heated. When the preparations are stored, especially in the summer months, they are gradually transformed into light-yellow crystalline substances, impregnated with liquid. The hydrobromide of the dianil of  $\beta$ -phenoxyglutamic aldehyde is somewhat more stable. However, it also decomposes when stored for a long time or when heated.

A study of the crystalline products, obtained as a result of the transformation of the salts of the dianils (III;  $\text{Ar} = \text{C}_6\text{H}_5-$ ,  $R = -, \text{OAlk}, -\text{OC}_6\text{H}_5$ ), revealed that they are all the same substance, namely, the bromophenylate of  $\gamma$ -phenylaminopyridine (IV) (bright yellow hygroscopic needles), M. p. 192-193°.

• This circumstance was apparently the reason for the unsuccessful experiments of Ebert on the cleavage of  $\gamma$ -methoxypyridine with cyanogen bromide and aniline. He was unable to isolate the hydrobromide of the dianil of  $\beta$ -methoxyglutamic aldehyde [3].

Found %: N 8.52; 8.39; Br 24.45; 24.68  $C_{17}H_{15}N_2Br$ . Calculated %: N 8.57; Br 24.44

The formation of compound IV proceeds by the general scheme:



In the case of  $\beta$ -phenoxy derivative III it was found that phenol is present in the transformation products. As a result, the reaction discovered by Zincke for the cyclization of the salts of glutaric aldehyde dianils into N-arylpipridinium salts, taking place under comparatively drastic conditions (fusion, heating with concentrated hydrochloric acid, etc.) [4], proceeds with unusual ease in the given instance.

The studied transformations can be regarded as being a particular case of the general reaction for the replacement of  $\gamma$ -alkoxy (phenoxy) groups by aromatic amines in pyridinium salts containing electronegative radicals ( $C_6H_5(NO_2)_2^-$ ,  $C_6H_5^-$ ) on the cyclic nitrogen atom (cf. [1]). Undoubtedly, here there is conjugation of the p-electrons of the oxygen atom in the  $-OAlk$  ( $-OC_6H_5$ ) with the remaining portion of the pyridinium salt molecule (see, for example, V), which imparts the character of oxonium salts (see [5]) to these compounds.

The hydrobromide of the  $\beta$ -methylmercaptoglutaric aldehyde dianil (III;  $Ar = C_6H_5^-$ ,  $R = -SCH_3$ ), shows a great tendency for cyclization. However, here the reaction does not stop at the stage of forming the bromophenylate of the  $\gamma$ -methylmercaptopyridine. Such a reaction course becomes understandable if we consider that the sulfur atom in the  $\gamma$ -methylmercaptopyridine bromophenylate is partially found in the onium state (see V), and that sulfonium salts are characterized by a lower reactivity than are oxonium salts.

An increase in the electronegative character of the radical attached to the nitrogen atom in  $\gamma$ -methylmercaptopyridine leads to exchange of the methylmercapto group by an amine radical: the chloro-(2,4-dinitrophenylate of  $\gamma$ -methylmercaptopyridine reacts with aromatic amines, although at a somewhat slower rate than do the  $\gamma$ -alkoxy derivatives (see [1]).

We became interested in the question of the mobility of the alkoxy groups found in the alkyl halide salts of the  $\gamma$ -alkoxypyridines. Here it was found that the reaction of  $\gamma$ -methoxypyridine methiodide with aniline (in alcohol solution with heating on the water bath) results in the cleavage of methyl iodide and the formation of N-methyl- $\gamma$ -pyridone. Here the presence of  $\gamma$ -phenylaminopyridine methiodide could not be shown.

Consequently, to impart to alkoxy groups the ability to be replaced it is insufficient to have only transition of the cyclic nitrogen atom into the tetravalent state, but in addition, it is necessary to have an electronegative radical present on this atom.

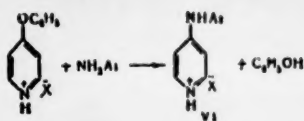
Next we studied the ability of the phenoxy group in  $\gamma$ -phenoxypyridine methiodide to be replaced by the radicals of aromatic amines. The cleavage of aryl halide (under the influence of an aromatic amine) in the given case seemed highly improbable. When  $\gamma$ -phenoxypyridine methiodide was heated with aniline (115-120°) we obtained the methiodide of  $\gamma$ -phenylaminopyridine (yield ~88%).

Later it was found that replacement of the phenoxy group by an aromatic amine radical is easily accomplished if a mixture of the  $\gamma$ -phenoxypyridine hydrohalide and the aromatic amine is heated, and also if the salt of the aromatic amine is heated with  $\gamma$ -phenoxypyridine. However, the phenoxy group is not replaced when a mixture of the salts of  $\gamma$ -phenoxypyridine and the aromatic amine is heated.

From this it follows that the  $\gamma$ -phenoxypyridinium cation and the free amine take part in the reaction:

\* After drying in vacuo at 40-50°.





Ar :  $C_6H_5$  — (84–96), (n)  $CH_3C_6H_4$  — (86), (o)  $CH_3C_6H_4$  — (~58),  
 (n)  $ClC_6H_4$  — (~73), (n)  $CH_3OC_6H_4$  — (83),  $\alpha$  —  $C_{10}H_7$  — (42)\*

Naturally the thought arose of reacting  $\gamma$  phenoxy pyridine with the salts of aliphatic amines and with the simpler ammonium salts. When this was done it was found that the phenoxy group can be replaced in similar manner by the amino group and by the radicals of primary and secondary aliphatic amines. Thus, the fusion of  $\gamma$ -phenoxy pyridine with cyclohexylamine hydrobromide (200–210°, 1 hour) gave  $\gamma$ -cyclohexylaminopyridine (72% yield). Colorless prisms (from ether). M.p. 147–148°.

Found %: N 15.87; 16.05  $C_{11}H_{15}N_2$ . Calculated %: N 15.90

$\gamma$  Dimethylaminopyridine was synthesized in a similar manner (190–200°, 1 hour). Yield 82%. Colorless plates with m.p. 112–113°. The picrate had m.p. 204–206° (see [6]).

Next it was found that the heating of  $\gamma$ -phenoxy pyridine with ammonium chloride in an open vessel (300–310°, 1 hour) readily gave  $\gamma$ -aminopyridine (yield 90–95%); to extract the  $\gamma$ -aminopyridine from the water solution we used n-butanol, which greatly simplifies the isolation of this base.

On the score of simplicity and convenience of the operations the preparation of  $\gamma$  aminopyridine by the above method is far superior to the known syntheses of Koenigs and Greiner [7] and of Hertog and Overhoff [8], which because of a number of limitations are practically valueless for the synthesis of amino-substituted pyridines. In contrast to this, the reaction studied by us can serve as a convenient general method for the preparation of various  $\gamma$ -amino-substituted pyridines.

It should be mentioned that the behavior of  $\gamma$ -phenoxy pyridine in its reaction with amine salts is similar to that of 9-phenoxyacridine [9]. However, it was difficult to predict this analogy, since it is known that the 9-alkoxy acridines react differently with amine salts than do the  $\gamma$ -alkoxy substituted pyridines and quinolines [10].

Toward the end of our investigation there appeared a paper by Jerchel and coworkers, devoted to the reactions of the  $\gamma$ -pyridylpyridinium salts [11]. The German investigators, proceeding from different considerations, came to the conclusion that it is possible to synthesize  $\gamma$ -aminopyridine by the reaction of  $\gamma$  phenoxy pyridine with ammonia. However, a description of these experiments is absent in the experimental portion of their paper.

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# THE PROBLEM OF THE GRAPHITIZATION OF CARBONIFEROUS SUBSTANCES

A. M. Subko and E. Z. Spektor

(Presented by Academician G. V. Kurbyumov, November 14, 1956)

In the x-ray study of coke graphitization it was revealed that the x-ray patterns of specimens, burned at 1700-1800°, show narrow lines, which are situated at angles of 22°35' (intense line), 33° (weak line) and 41°45' (intense line). As can be seen from Fig. 1 and Table 1, the position of these lines does not coincide with either the position of the  $\alpha$ -graphite lines or the position of the lines characteristic for  $\beta$ -graphite. The angular position of the graphite lines was calculated for both the interlayer distance in the graphite crystal  $d = 3.35$  Å and for  $d = 3.42$  Å, characteristic for the reticular structure of carbon.

TABLE 1

Indices of the graphite	Graphite modification	$\theta$ for $d=3.35$ Å	$\theta$ for $d=3.42$ Å	$\theta$ of addit. lines observed on photos	Indices of a solution of Si in Fe	Lattice parameter	Silicon concentration, %
002	$\alpha + \beta$	13°20'	13°				
100	$\alpha$	21°10'	21°10'				
10 <sup>3</sup> / <sub>2</sub>	$\beta$	21°46'	21°39'				
101	$\alpha$	22°20'	22°15'				
10 <sup>3</sup> / <sub>4</sub>	$\beta$	23°14'	23°	22°36'	110	2.84	13
004	$\alpha + \beta$	27°18'	26°44'				
110	$\alpha + \beta$	38°44'	38°44'	~33°	200		
112	$\alpha$	41°48'	41°40'	41°43'	211	2.84	13
006	$\alpha + \beta$	43°42'	42°24'				

The fact that the position of the above indicated lines is close to the position of the lines for graphite (the lines situated at an angle of 22°35' to the graphite line (101) and at an angle of 41°45' to the graphite line (112)), apparently caused some investigators to consider these lines as belonging to a special graphite modification. Thus, in paper [1] it is stated that the  $\beta$ -graphite modification was prepared artificially by the burning of petroleum coke, with its  $a$  and  $c$  parameters being greater than for natural  $\beta$ -graphite. In paper [2] some data are presented, from which it is concluded that the temperature at which graphitization of the carboniferous substances studied by the author commences is equal to 1700°. Both of these conclusions are in discord with the experimental data given in the literature on the graphitization of carboniferous substances. In a number of studies [3, 4] it was shown that with a relatively large change in parameter  $c$  for various carboniferous substances as a function of the conditions for their formation (coals with different degrees of metamorphism, peats, soots, cokes, etc.) the  $a$  parameter remains constant and is equal to 1.42 Å for extremely different carboniferous substances. The data given in [5] are also quite convincing, in accord with which the start of true graphitization occurs only at a temperature of 2000°. In these cases the x-ray patterns show broad maxima from the oblique graphite planes (101) and (112), while the maxima of (002) and (004) are shifted toward larger angles (during graphitization the distance between layers decreases from 3.42 Å to 3.36 Å).

The additional data, obtained by us in studying the graphitization of carboniferous substances, are discussed below. It seemed of interest to determine the nature of the noncarbon diffraction lines that appear on the x-ray photographs of cokes that had been burned at 1700-1800°. A study of a large volume of spectral analysis data, as well as a study after a very thorough ashing, revealed that traces of iron, silicon and aluminum are present

in carboniferous substances (coke). It was natural to assume in such case the presence of small amounts of iron, silicon and aluminum oxides in cokes. In accord with the physicochemical analysis data given in [6] there occurs intense reduction of silicon from its oxides by solid carbon at 1700-1800°. The presence of iron atoms in a carboniferous substance accelerates the silicon reduction process, accompanying it with the formation of FeSi. Taking these data into consideration, it could be postulated that the noncarbon lines, appearing on the x-ray photographs of cokes that had been burned at 1700-1800°, belong to the  $\alpha$ -solid solution of silicon in iron. To verify this postulation relative to the position of the lines on the roentgenograms (assuming them to be reflections of the (110), (200) and (211) planes of a body-centered lattice) we determined the lattice parameter. From the values of the latter we calculated the silicon concentration in a solution of Si in Fe, which for a number of specimens proved to be equal to 10-13%. This result is in good agreement with the equilibrium diagram for Fe-Si [6, 7], in accord with which the maximum amount of silicon in a solid solution of Si in Fe at room temperature is 13%.

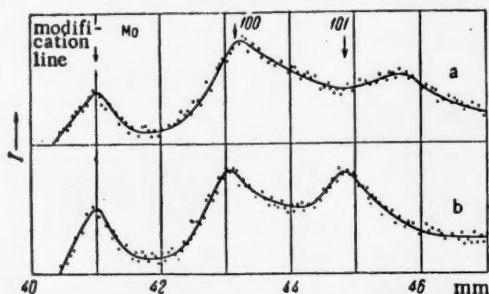


Fig. 1. Microphotograms of the 100 and 101 lines; a) is the line for the coke burned at 1700°, and b) is the line for graphite. Here and in Fig. 2 the distances from the center of the photograph are plotted along the abscissa.

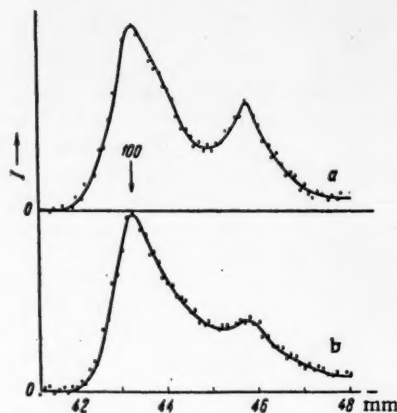


Fig. 2. Microphotograms: a) is the line of a coke that had been burned at 1700° and  $p = 400$  mm Hg pressure; b) is the line of the same coke that had been burned at 1700° and  $p = 40$  mm Hg pressure.

The postulation that a solid solution of silicon in iron is formed when cokes are burned at 1700-1800° is confirmed by the experiments made with cane carbon. We burned pure cane carbon and the same carbon with very small additions of iron and silicon oxides. Only the maxima for the (002), (100), (004) and (110) planes, characteristic for a reticular structure [4], appear on the roentgenogram of the pure cane carbon, while the roentgenograms of the cane carbon with small additions of iron and silicon oxides also show distinct lines that have angles of 22°36' and 41°44'. The lines of the  $\alpha$ -solid solution of silicon in iron do not appear when the burning temperatures are raised to 1900-2000°. This can be explained by the fact that at temperatures of 1900-2000° the vapor pressure, and consequently also the evaporation rate, of the solid solution increases sharply [6]. Here the evaporation rate increases with decrease in the external pressure, which can be seen from Fig. 2, where the microphotograms of the roentgenograms in the region of the angles ranging from 20 to 23° are shown.

All of the data presented above unanimously support the postulation that the lines, appearing on the roentgenograms of the cokes and other carboniferous substances that had been burned at 1700-1800°, belong to the  $\alpha$ -solid solution of Si in Fe. It is not only in the burning of cokes under laboratory conditions that the formation of a solid solution of silicon in iron is observed at temperatures of 1700-1800°. The x-ray patterns of coke samples, taken from blast-furnace hearths, also show quite intense lines with the angles: 22°28' - 22°40'; 32°40' - 33°; 41°40' - 41°46'.

#### SUMMARY.

It was shown that the burning of coke specimens at temperatures of 1700-1800° is accompanied by the formation of the  $\alpha$ -solid solution of silicon in iron. The x-ray patterns in these cases show narrow lines with the angles 22°35', 33° and 41°45'.

In studying the graphitization of carboniferous substances at temperatures above 1600° the possibility of forming in these substances a solid solution of silicon in iron should be taken into consideration. The angular position of the diffraction lines for the solid solution is close to that of the lines for graphite, which can serve as a source of erroneous conclusions relative to the character of graphitization.

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# SYNTHESIS OF THE ANALOGS OF METHYLHEPTENONE AND METHYLHEPTADIENONE

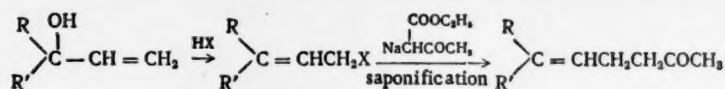
Academician I. N. Nazarov, S. M. Makin, V. B. Mochalin

D. V. Nazarova, V. P. Vinogradov, B. K. Kruptsov,

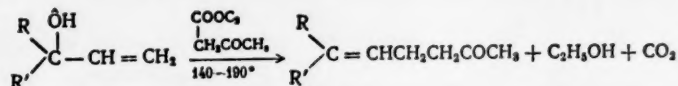
I. I. Nazarova and O. A. Shavrygina

The synthesis of the analogs of methylheptenone and methylheptadienone is of interest for obtaining the corresponding analogs of linalool, geraniol, citral, dehydrocitral, farnesol, ionone and other natural isoprenoid compounds. The starting acetylene alcohols, needed for the mentioned syntheses, were obtained by a method that was developed in our laboratory, namely, by the condensation of ketones with acetylene in the presence of powdered potassium hydroxide under pressure [1]. When selectively hydrogenated in the presence of palladium on calcium carbonate the acetylene alcohols are almost quantitatively converted to the corresponding vinyl alcohols [2], while the latter are converted to the corresponding analogs of methylheptenone by three different methods, as had been described in an earlier communication [3].

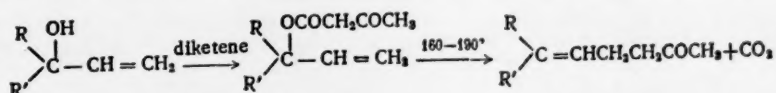
**Method A.** The treatment of tertiary vinyl alcohols with either gaseous hydrogen chloride or hydrogen bromide at 0-20° readily yields primary halides of the allyl type [4], the condensation of which with sodio-acetoacetic ester, followed by saponification, gives the analogs of methylheptenone in an overall yield of 70-75%, based on the vinylcarbinols taken for reaction:



**Method B.** At a temperature of 140-190° the tertiary vinyl alcohols react directly with acetoacetic ester, in which connection ethyl alcohol and carbon dioxide are evolved in nearly theoretical amount, and the analogs of methylheptenone are formed in 60-70% yield [5]:



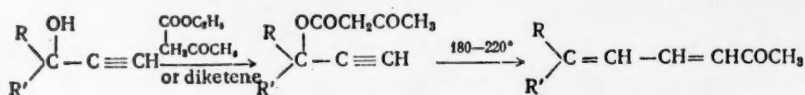
**Method C.** The treatment of tertiary vinyl with diketene in the presence of small amounts of either triethylamine or piperidine yields the acetoacetic esters of these alcohols in 80-90% yield (Table 2), the pyrolysis of which at 160-190° also leads to the formation of the analogs of methylheptenone in 70-75% yield [6]:



The 2,3-dimethyl-2-hepten-6-one (IV) needed for the synthesis of irone was obtained in 60-75% yield by all three methods described above.

The starting dimethylisopropenylcarbinol was obtained by reacting methyl lithium with methyl methacrylate.

We also made a detailed study of the synthesis of the analogs of methylheptadienone by methods B and C. The heating of tertiary acetylenic alcohols with acetoacetic ester, as well as the pyrolysis of the acetoacetic esters of these alcohols, obtained with the aid of diketene (Table 2), makes it possible to obtain the analogs of methylheptadienone in 60-70% yield [7]:



All of the analogs of methylheptenone (except ketones I-IV) and of methylheptadienone obtained by us are summarized in Table 1.

Allylacetone (I) [9], crotylacetone (II) and chlorocrotylacetone (III) [8] were obtained in about 70% yield only by method A, namely, by the reaction of the corresponding halo derivatives with sodioacetoacetic ester.

It should be mentioned that in the case of vinylcyclopentanol the yield of the unsaturated ketone (X) by methods B and C is greatly reduced due to a different direction for the pyrolysis of the acetoacetic ester, leading to the formation of acetone and the hydrocarbon: (1-vinyl- $\Delta^2$ -cyclopentene).

**Dimethylisopropenylcarbinol.** To an ether solution of methyl lithium, prepared from 9.1 liters of lithium and 91 g of methyl iodide in 400 ml of dry ether, at  $-10^\circ$  in two hours was added 25 g of methyl methacrylate in 70 ml of ether, and then the reaction mass was heated for 40 minutes at ether boil.

The lithium alcoholate was decomposed with ice-cold water under cooling, and the ether layer was separated, dried over potash, and distilled. We obtained 20.3 g (81%) of dimethylisopropenylcarbinol with b.p. 115-116°;  $n_D^{20}$  1.4320;  $d_4^{20}$  0.8437; -MR found 30.67; calculated 30.96.

Found %: C 72.00; H 12.00  $\text{C}_6\text{H}_{12}\text{O}$ . Calculated %: C 72.12; H 11.95

Labile hydrogens found 1.00; 0.96.

**Dimethylisopropenylcarbinol Acetoacetate.** To a mixture of 15 g of dimethylisopropenylcarbinol and 5 drops of triethylamine at 60-70° was added 15 g of diketene in 15 minutes. The mixture was heated for 2.5 hours at 80°, then dissolved in ether, the ether solution washed with 5% bicarbonate, dried over magnesium sulfate, and distilled. We obtained 26.2 g (95%) of dimethylisopropenylcarbinol acetoacetate with b.p. 68-69°/2 mm;  $n_D^{20}$  1.4479;  $d_4^{20}$  0.9915; MR found 49.56; calculated 49.58.

Found %: C 65.32; 65.25; H 8.62; 8.37  $\text{C}_{10}\text{H}_{16}\text{O}_3$ . Calculated %: C 65.22; H 8.70

**Dimethylheptenone (IV).** Method A. To the sodioacetoacetic ester, prepared from 1100 ml of methanol, 60 g of metallic sodium and 365 g of acetoacetic ester, with stirring and cooling was added in 85 minutes 415 g of 2,3-dimethyl-4-bromo-2-butene (b.p. 69-71°/40 mm), obtained by saturating 230 g of 2,3-dimethylbutadiene (without solvent) with dry hydrogen bromide at  $-5^\circ$ . The mixture was stirred for 3 hours at 65°, the methanol was removed by distillation under slight vacuum, and the residue was heated with a solution of 120 g of sodium hydroxide in 800 ml of water for 3 hours at 70°. The reaction mass was acidified under cooling with hydrochloric acid, the product extracted with ether, dried over magnesium sulfate, and distilled. We obtained 278 g (79%) of dimethylheptenone (IV) with b.p. 78-80°/15 mm;  $n_D^{20}$  1.4500;  $d_4^{20}$  0.8688; MR found 43.33; calculated 43.30 [10]. In similar manner the reaction of Na acetoacetic ester with crotyl bromide gave crotylacetone (V) in 63% yield, with b.p. 75-77°/60 mm;  $n_D^{20}$  1.4292;  $d_4^{20}$  0.8442; MR calculated 34.07 (11).

**Method C.** Dimethylisopropenylcarbinol acetoacetate (18.4 g) was heated at 170-175° for 45 minutes. Here 2330 ml of carbon dioxide was evolved. The product was vacuum-distilled to give 8.4 g (60%) of dimethylheptenone (IV) with b.p. 78-80°/15 mm;  $n_D^{20}$  1.4500.

TABLE 1

Expt. Nos.	Formula and constants: b.p. °C/mm; $n_D^{20}$ ; $d_4^{20}$	Yield, %			Found %		Calcu- lated		Semicarbazone of 2,4- dinitrophenylhydrazine		
		A	B	B	C	H	C	H	m.p. °C	N, %	
										found <sup>2</sup>	calcd.
V	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{COCH}_3$ 75-77/11; 1.4420; 0.8603	73	—	62	77.18	11.34	77.08	11.51	113-114 <sup>a</sup>	21.31 <sup>a</sup>	21.32 <sup>a</sup>
VI	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{COCH}_3$ iso-C <sub>6</sub> H <sub>5</sub> 85-87/10; 1.4445; 0.8570	76	—	60	77.84	11.41	77.93	11.60	60-61 <sup>a</sup>	17.48 <sup>a</sup>	17.40 <sup>a</sup>
VII	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{COCH}_3$ tert -C <sub>6</sub> H <sub>5</sub> 96-98/16; 1.4488; 0.8557	70	60	72	78.80	12.06	78.57	11.90	124 <sup>a</sup>	19.80 <sup>a</sup>	19.90 <sup>a</sup>
VIII	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{COCH}_3$ iso -C <sub>6</sub> H <sub>5</sub> 120/25; 1.4466; 0.8496	82	70	80	79.33	12.20	79.05	12.16	58 <sup>a</sup>	16.64 <sup>a</sup>	16.77 <sup>a</sup>
IX	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{COCH}_3$ 64-66/1; 1.4780; 0.9848	68	72	71	79.40	10.95	79.50	10.85	158-159 <sup>a</sup>	18.40 <sup>a</sup>	18.60 <sup>a</sup>
X	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{COCH}_3$ 73-75/2; 1.4790; 0.9250	—	40	16	79.19	10.56	79.00	10.50	94-96 <sup>a</sup>	16.08 <sup>a</sup>	16.07 <sup>a</sup>
XI	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$ 83-84/10; 1.5161; 0.8943	—	—	61	78.30	10.03	78.21	10.21	148 <sup>a</sup>	17.68 <sup>a</sup>	17.68 <sup>a</sup>
XII	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$ iso -C <sub>6</sub> H <sub>5</sub> 103-104/11; 1.5166; 0.8904	—	—	59	78.92	10.48	79.80	10.50	84 <sup>a</sup>	15.54 <sup>a</sup>	15.46 <sup>a</sup>
XIII	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$ iso -C <sub>6</sub> H <sub>5</sub> 78-80/1; 1.5160; 0.8030	—	69	60	79.42	10.94	79.52	10.84	78 <sup>a</sup>	16.15 <sup>a</sup>	16.26 <sup>a</sup>
XIV	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$ iso -C <sub>6</sub> H <sub>5</sub> 66-67/0.2; 1.4925; 0.8783	—	56	62	80.14	11.03	79.93	11.18	161 <sup>a</sup>	20.24 <sup>a</sup>	20.08 <sup>a</sup>
XV	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$ 98-100/1; 1.5290	—	37	38	80.31	9.61	80.50	9.75	194 <sup>a</sup>	18.85 <sup>a</sup>	18.83 <sup>a</sup>
XVI	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$ 75-77/1; 1.5258	—	13	14	79.80	9.26	80.00	9.33	186 <sup>a</sup>	17.83 <sup>a</sup>	17.70 <sup>a</sup>
									203 <sup>a</sup>	15.81 <sup>a</sup>	15.53 <sup>a</sup>
									183 <sup>a</sup>	16.10 <sup>a</sup>	16.27 <sup>a</sup>
									108 <sup>a</sup>	16.95 <sup>a</sup>	17.27 <sup>a</sup>

<sup>1</sup>A, B and C — methods of preparation.<sup>2</sup>Duplicate analyses are always omitted.<sup>3</sup>The data relate to the semicarbazone.<sup>4</sup>The data relate to the 2,4-dinitrophenylhydrazone.

**Cyclohexylidenepentanone (IX). Method B.** A mixture of 207 g of vinylcyclohexanol and 224 g of acetoacetic ester was heated for 7 hours with gradual elevation of the temperature from 134 to 198°. Here 28.7 liters of carbon dioxide was evolved and 89.7 g of ethyl alcohol, containing as impurity some 1-vinyl-Δ<sup>1</sup> cyclohexene with b.p. 72-78°, was distilled. Vacuum-distillation of the residue gave 194 g (72%) of 1-cyclohexylidene-4-pentanone with b.p. 64-66°/1 mm;  $n_D^{20}$  1.4770.

**Tert-butylheptadienone (XIII). Method B.** A mixture of 12.6 g of methyl-tert-butylethynylcarbinol (b.p. 141-142°) and 13 g of acetoacetic ester was heated for 3 hours at 190-220°. Here 2200 ml of carbon dioxide was evolved, and 6.9 ml of liquid with b.p. 70-77° was distilled.

TABLE 2

Expt. Nos.	RR'	b.p. °C/mm	$n_D^{20}$	$d_4^{20}$	MR*		Found%		Yield, %*		Yield, %
					found	calc.	C	H	C	H	

Vinylcarbinol acetoacetates of general formula					$\begin{array}{c} \text{OCOCH}_3\text{COCH}_3 \\   \\ \text{R} \\   \\ \text{R}'\text{C}-\text{CH}=\text{CH}_2 \end{array}$						
XVII	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub>	62-63/0.5	1.4429	0.9809	49.78	49.58	65.48	8.59	65.19	8.75	82
XVIII	CH <sub>3</sub> , iso-C <sub>2</sub> H <sub>5</sub>	70-72/0.5	1.4478	0.9760	54.36	54.20	66.88	9.32	66.64	9.15	81
XIX	CH <sub>3</sub> , tert-C <sub>4</sub> H <sub>9</sub>	90-91/4	1.4552	0.9736	59.10	59.42	68.00	9.67	67.92	9.43	83
XX	iso-C <sub>2</sub> H <sub>5</sub> , iso-C <sub>4</sub> H <sub>9</sub>	87-89/1.5	1.4586	0.9773	63.37	63.43	69.28	9.97	69.00	9.80	80
XXI	(CH <sub>3</sub> ) <sub>2</sub>	100-103/1	1.4730	—	—	—	68.41	8.72	68.60	8.58	89
XXII	(CH <sub>3</sub> ) <sub>3</sub>	87/1	1.4571	—	—	—	67.42	8.17	67.40	8.16	78

Ethynylcarbinol acetoacetates of general formula					$\begin{array}{c} \text{OCOCH}_3\text{COCH}_3 \\   \\ \text{R} \\   \\ \text{R}'\text{C}-\text{C}\equiv\text{CH} \end{array}$						
XXIII	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub>	73-74/1	1.4488	1.0150	48.11	48.04	65.97	7.54	65.91	7.74	85
XXIV	CH <sub>3</sub> , iso-C <sub>2</sub> H <sub>5</sub>	77-78/1	1.4511	1.0046	52.61	52.66	67.43	8.13	67.33	8.22	87
XXV	CH <sub>3</sub> , tert-C <sub>4</sub> H <sub>9</sub>	90-91/4	1.4560	0.9940	57.42	57.21	68.40	8.74	68.57	8.57	82
XXVI	iso-C <sub>2</sub> H <sub>5</sub> , iso-C <sub>4</sub> H <sub>9</sub>	89-90/1.5	1.4616	0.9970	61.91	61.83	69.52	8.97	69.61	8.98	82
XXVII	(CH <sub>3</sub> ) <sub>2</sub>	99-100/1	1.4785	—	—	—	69.05	7.72	69.25	7.70	84
XXVIII	(CH <sub>3</sub> ) <sub>3</sub>	90-91/1	1.4782	—	—	—	68.12	7.52	68.00	7.22	92

\* The MR's are always calculated for the keto form.

\*\* Duplicate analyses are always omitted.

Vacuum-distillation of the residue gave 11.5 g (69%) of tert-butylheptadienone (XIII) with b.p. 77-80°/1 mm;  $n_D^{20}$  1.5160.

**Method C.** Methyl-tert-butylethynylcarbinol acetoacetate (9.6 g) (b.p. 90-94°/4 mm) was heated for 1.5 hours at 200-220°. Here 1020 ml of carbon dioxide was evolved. Vacuum-distillation of the residue gave 4.5 g (60%) of tert-butylheptadienone (XIII) with b.p. 83-85°/4 mm;  $n_D^{20}$  1.5160.

The other compounds, presented in Tables 1 and 2, were obtained in a similar manner.

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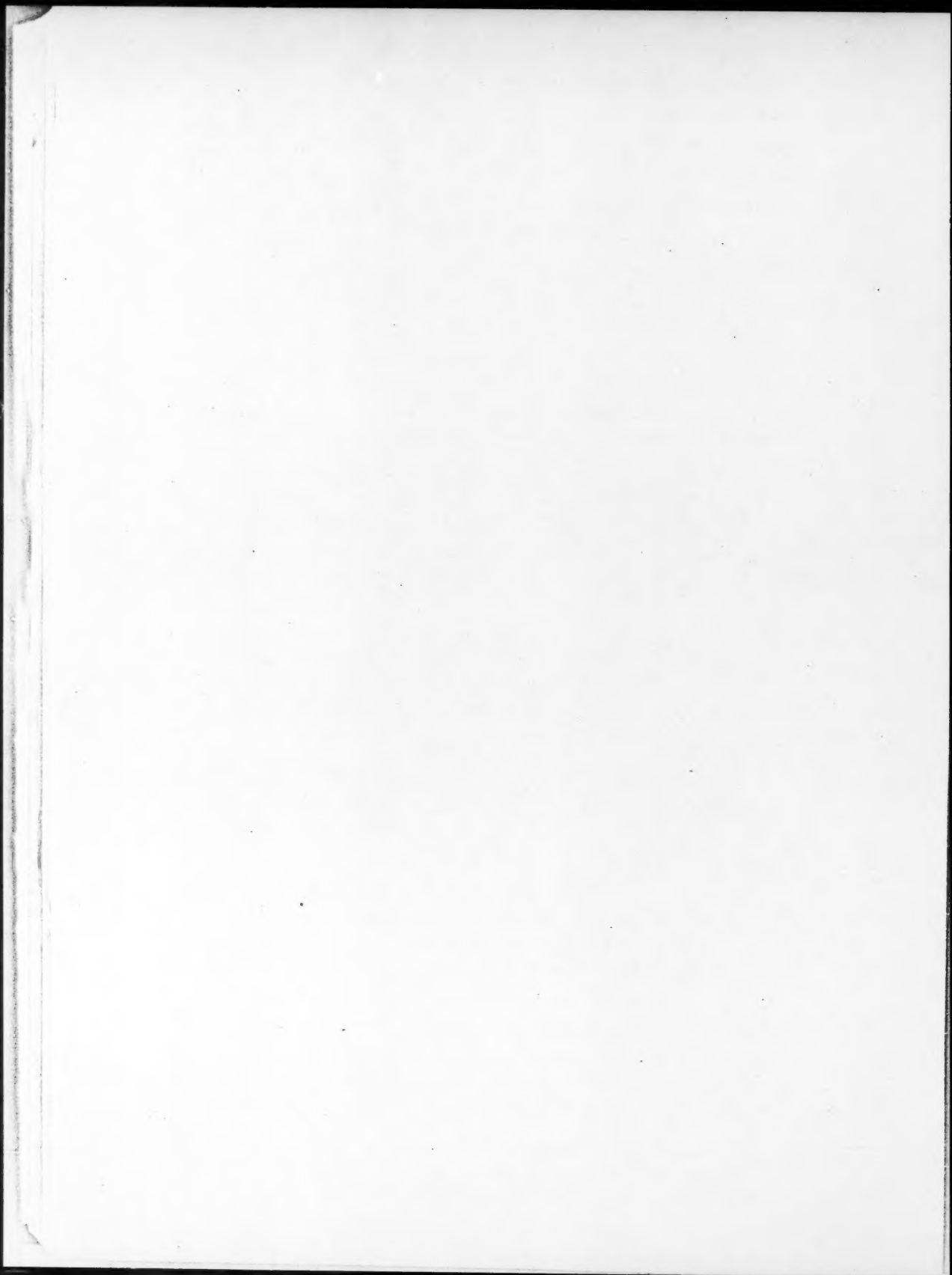
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## EQUILIBRIUM OF TWO LIQUID PHASES IN THE SIMPLER FLUORINE SILICATE SYSTEMS

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(Presented by Academician D. S. Korzhinsky, January 31, 1957)

The stratification of fluorine-containing silicate melts into two immiscible liquids was first observed by D. P. Grigoryev [1]. The formation of two liquid phases in silicate melts, containing phosphates and fluorides, was revealed by V. V. Lapin [2] in a microscopic study of slags. Later, Oelsen and Maetz [3] and Fischer [4] occupied themselves with a study of stratification in silicate melts containing fluorides.

In all of these studies the formation of volatile  $\text{SiF}_4$  ( $2\text{CaF}_2 + \text{SiO}_2 \rightleftharpoons 2\text{CaO} + \text{SiF}_4$ ) greatly complicated the experimentation and excluded the possibility of studying the side binary systems  $\text{SiO}_2$ -metal fluorides.

We made numerous attempts to run the fusion of fluosilicate melts in molybdenum crucibles, sealed in quartz ampoules. The latter however, even at comparatively low temperatures became plastic and exploded. Later it was found that  $\text{SiO}_2$  reacts with  $\text{SiF}_4$ .

V. A. Dunaevsky suggested running the fusions in molybdenum crucibles, fitted with molybdenum stoppers - rivets. It was found that after some practice it is possible to rivet the molybdenum crucible (Fig. 1, A) in such a manner that there is practically no evaporation of  $\text{SiF}_4$  when silicate-fluoride mixtures are heated. The dimensions of the crucibles can be changed within fairly wide limits, but the internal diameter should not be too great, since then the riveting becomes difficult.

From 0.02 to 0.10 g of a finely divided mixture of fluoride and quartz was placed in the crucible, which was then riveted and suspended in a furnace with a molybdenum heater [5]. The temperature was measured with an optical pyrometer, and the heating (usually 5-15 minutes) was run in a hydrogen atmosphere. Cooling was effected by casting the crucible into the cold portion of the furnace or by simply turning the heat off (the cooling rate of the furnace at  $1700^\circ$  was about  $150^\circ$  a second).

The crucible after the heating was weighed and broken open. The fusions were considered satisfactory if the weight losses did not exceed 1.0-1.5% of the batch weight. The existence of two liquid phases in the various mixtures was decided by a microscopic investigation of the immersion compounds. If two liquid phases had been formed in the crucible at elevated temperature, then the same indications of two immiscible liquids in the immersion compounds was observed as in the case of the stratification of acid silicate melts, first revealed by Greig [6]. One of the liquids gives a glass with a low refraction, while the second liquid forms spherical or oval inclusions in it. These inclusions almost always show partial crystallization. Only the extremely fine inclusions form a pure glass. For the mixtures, the composition of which was at some distance from the boundary of the equilibrium region of two liquid phases, the stratification was quite distinct. In measure with increase in the fluoride content the composition of the mixture approached the boundary of the stratification region and the amount of liquid, consisting mainly of silica, decreased, and the microscopic study became more difficult. Small amounts of the low-refractive glass with characteristic inclusions could have remained unnoticed. In connection with this the concentration boundary of the stratification region could not be established with an accuracy of less than 2%.

From a summary of the results, presented in Table 1, it can be seen that the regions of two liquid phases in the systems fluoride-silica are very large. They greatly exceed the corresponding stratification regions in the systems oxides-silica. Two liquid phases are not formed in the system  $\text{BaO-SiO}_2$ , while a broad break in

the miscibility in the liquid state is observed in the system  $\text{BaF}_2\text{-SiO}_2$ . At the same time the formation of immiscible liquids was not observed in the melts composed of various mixtures of silica and the fluorides of lithium, sodium and aluminum.

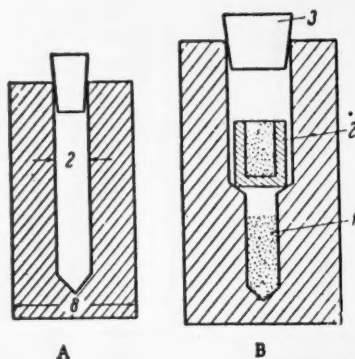


Fig. 1. A—molybdenum crucible with rivet. B—molybdenum crucible for studying the reaction of  $\text{SiO}_2$  with  $\text{SiF}_4$ .

TABLE 1  
Equilibrium of Two Liquid Phases in Silica-Metal Fluoride Systems

Fluorides	Stratification boundary*		Ratio of cation radius to valence, A	Temp. of stratification near boundary, °C
	wt. %	mole %		
$\text{MgF}_2$	92	92	0.375	1430
$\text{CaF}_2$	94	92	0.505	1420
$\text{SrF}_2$	95	90	0.59	not determ.
$\text{BaF}_2$	95	86	0.68	1460
$\text{LiF}$	Stratification not observed		0.69	—
$\text{NaF}$	Likewise		0.98	—
$\text{AlF}_3$	• •		0.190	—

\* Composition of the liquid phase rich in cations.

The same as in ordinary silicate systems [7], the width of the stratification region in fluoride systems is associated with the size and charge of the cations. The stratification region increases with decrease in the ratio of the cation radius to its charge. An exception is aluminum, which is apparently associated with its amphoteric properties.

The compositions of the liquids containing much fluoride are given in Table 1. As regards the coexisting equilibrium liquids, a number of conclusions relative to their composition can be made from the following. Mixtures, containing only 2-3% fluorides and 97-98%  $\text{SiO}_2$ , had after fusion distinct indications of two liquid phases. As a result, one of the liquid phases consisted predominantly of  $\text{SiO}_2$  and contained less than 2-3% of the fluorides of the alkaline earth metals. With stratification in such systems as  $\text{CaO-SiO}_2$  and  $\text{MgO-SiO}_2$  one of the liquids consists mainly of  $\text{SiO}_2$  and forms a glass with a refractive index of 1.461-1.462, which testifies to the presence in it of a small amount of either  $\text{CaO}$  or  $\text{MgO}$  (the refractive index of pure quartz glass is 1.459 [6]). In our case the glasses, consisting mainly of  $\text{SiO}_2$ , had a much lower refractive index. Thus, the fusion of a mixture of 90%  $\text{SiO}_2$  + 10%  $\text{CaF}_2$  gave an acid glass with a refractive index of 1.442. Such a substantial reduction in the refractive index of the glass cannot be due to the dissolving of  $\text{CaF}_2$  in it.\* The low refractive index of the glasses caused us to postulate that  $\text{SiF}_4$  enters into the composition of the acid liquids and that the systems studied by us are reciprocal in nature (for example,  $\text{Ca, Si/F, O}$ ). This finds support in the fact that the temperature of the liquids in the stratification region does not remain constant, as should be the case in binary systems, but instead decreases with increase in the amount of fluorides. Mixtures, containing 5-10% fluoride, form two liquid phases only at 1600-1650°C. The temperatures (1420-1460°), at which two liquid phases are formed from mixtures whose compositions lie close to the boundary (from the fluoride side) of the stratification region, are given in Table 1.

In addition, the formation of comparatively low melting liquids when  $\text{SiO}_2$  is treated with  $\text{SiF}_4$  was confirmed by special experiment. A mixture of  $\text{CaF}_2$  +  $\text{SiO}_2$  (1) was placed on the bottom of a molybdenum crucible (Fig. 1, B), and a small amount of ground quartz was placed over it,

\* If it is assumed that a linear relationship exists between the refractive index and the amount of  $\text{CaF}_2$  in a glass, then the observed reduction in the light refraction could have been due to the presence of 68%  $\text{CaF}_2$ .

the latter did not come in contact with the crucible containing the  $\text{CaF}_2$ . The crucible charged in this manner was closed with a molybdenum rivet (3) and then heated at  $1460^\circ$  for 1 hour. It was found that the quartz in the small crucible melted on the surface and formed a glass with refractive index 1.445-1.452. As a result, the fusion of the quartz at  $1460^\circ$  (instead of at  $1715^\circ$ ) was due to reaction with the  $\text{SiF}_4$  formed in the heating of  $\text{CaF}_2 + \text{SiO}_2$ .

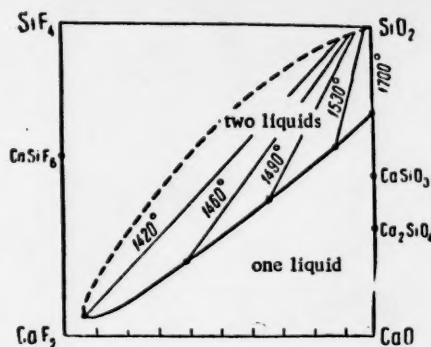


Fig. 2. Region of two liquid phases in the system  $\text{CaO}$ ,  $\text{CaF}_2/\text{SiO}_2$ ,  $\text{SiF}_4$ .

$\text{CaF}_2$ - $\text{SiF}_4$ - $\text{SiO}_2$  was not determined. It is shown in the plot by the dotted line, since this seemed most probable to us.

Taking into consideration the similarity in the  $\text{F}^-$  and  $\text{OH}^-$  ions, it can be assumed that such water-silicate systems as  $\text{H}_2\text{O}$ - $\text{CaO}$ - $\text{SiO}_2$  or  $\text{Ca}(\text{OH})_2$ - $\text{CaO}$ - $\text{SiO}_2$  are constructed in the same manner as the reciprocal system shown above. The investigations of Tuttle and England [8], who observed the melting of quartz when it was heated with steam under high pressure (up to 2000 atm.) at  $1300^\circ$ , can serve to lend some support to such an assumption. The glass obtained on cooling analyzed 98%  $\text{SiO}_2 + 2\% \text{H}_2\text{O}$ . Possibly the melt, forming this glass, should be regarded as being a solution of  $\text{SiO}_2 + \text{Si}(\text{OH})_4$ .

The series of fusions made by us of  $\text{CaF}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2$  mixtures made it possible to determine the boundary of the region of two liquid phases in this system (approximately assuming it to be a ternary system). It was found that here, the same as in the system  $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ , the presence of  $\text{Al}_2\text{O}_3$  results in a substantial contraction of the region of two liquid phases. The mixtures 25%  $\text{CaF}_2 + 75\% \text{SiO}_2$  and 50%  $\text{CaF}_2 + 50\% \text{SiO}_2$  form two liquids in the presence of 7.5 and 10%  $\text{Al}_2\text{O}_3$  respectively, but become homogeneous after the addition of 10.0 and 15.0%  $\text{Al}_2\text{O}_3$ . The configuration of the stratification region in the system  $\text{CaF}_2$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  is similar to that for  $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ , but it is much larger in the first system than in the second.

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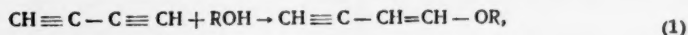
# THE REACTION OF DIACETYLENE WITH SOME HYDROXYL-CONTAINING COMPOUNDS

M. F. Shostakovsky, A. V. Bogdanova and G. K. Krasilnikova

(Presented by Academician B. A. Kazansky, February 9, 1957)

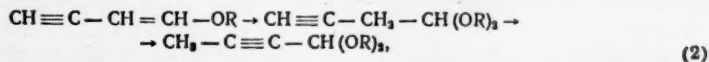
Diacetylene, because of its great reactivity, is of interest to synthetic organic chemistry. However, its use is limited by its difficult availability. Three methods are known for the preparation of diacetylene. The multistage and complex process of Bayer [1] can hardly be recommended even for laboratory preparation. In Germany, diacetylene is obtained as a by-product in the manufacture of acetylene by the arc process [2]. The method described by Herberts [3, 4] is quite acceptable, consisting in the chlorination of 2-butyne-1,4-diol and subsequent dehydrochlorination of the dichlorobutyne. The data given in the literature [5-7] on the reaction of diacetylene with alcohols is of a patent nature and does not contain a detailed description of the conditions used to run this reaction and the properties of the isolated products. The papers by Herberts [3] and Franke [8] present detailed studies in which the preparation of 1-methoxy-1-buten-3-yne its reaction with methanol and carbonyl compounds, and some of the transformations of the addition products obtained in this manner are described.

The purpose of the present study was to investigate the conditions for the reaction of diacetylene with butanol, cyclohexanol and  $\beta$ -decalol, the isolation of the products of this reaction, and a comparison of some of their properties. The reaction of diacetylene with alcohols proceeds under the influence of caustic alkalis with heating, and is accompanied by the formation of ethynylvinyl ethers [Equation (1)], in an excess of the alcohol passing into the acetals of 2-butyne-4-al [Equation (2)].



where  $\text{R} = \text{C}_4\text{H}_9$  (I);  $\text{C}_6\text{H}_{11}$  (II);  $\text{C}_{10}\text{H}_{17}$  (III).

where  $\text{R} = \text{C}_4\text{H}_9$  (I);  $\text{C}_6\text{H}_{11}$  (II);  $\text{C}_{10}\text{H}_{17}$  (III).



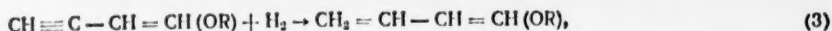
where  $\text{R} = \text{C}_4\text{H}_9$  (IV);  $\text{C}_6\text{H}_{11}$  (V);  $\text{C}_{10}\text{H}_{17}$  (VI).

where  $\text{R} = \text{C}_4\text{H}_9$  (IV);  $\text{C}_6\text{H}_{11}$  (V);  $\text{C}_{10}\text{H}_{17}$  (VI).

The reaction is stepwise, which is shown by the synthesis of the butynal acetals from the ethynylvinyl ethers and the alcohols in both alkaline and acid medium. In contrast to the alkylacetylenes, the first molecule of the alcohol adds to the acetylene in contradiction to the Markovnikov rule, which is due to the influence of the second ethynyl group. The next molecule of the alcohol adds to the ethynylvinyl ethers in accord with the Markovnikov rule, followed by isomerization in accord with that discovered by Favorsky for hydrocarbons [9]. When diacetylene is reacted with hydroxyl-containing compounds the absorption rate of the diacetylene depends on the starting compound and on the temperature. Only the formation of the ethynylvinyl ethers was observed when the heating was up to 100°. The acetals are formed in substantial amount at temperatures above 130°, and also when the amount of starting alcohol is increased. The reaction of diacetylene with  $\beta$ -decalol begins at 90° and is accompanied by the formation of only the ethynylvinyl ether; decalol was obtained at elevated temperatures; apparently the reaction proceeds up to the formation of the acetal (VI), which suffers decomposition when the mixture is worked up. The postulation that this butynal didecalyl acetal is unstable is quite probable, since even

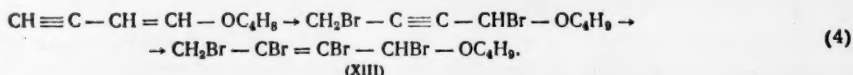


acetaldehyde didecyl acetal is an exceedingly unstable compounds, suffering decomposition when vacuum-distilled to yield  $\beta$ -decalol. We used bromination, hydrolysis [2] and hydrogenation (both partial and exhaustive) to prove the structure of the isolated ethers and acetals. With partial hydrogenation the 1-alkoxybutadienes are obtained [Equation (3)].

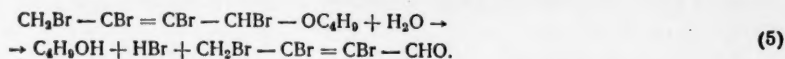


where  $\text{R} = \text{C}_{10}\text{H}_{17}$  (VII).

Exhaustive hydrogenation gave saturated ethers of the  $\text{C}_4\text{H}_9\text{OR}$ , series where  $\text{R} = \text{C}_4\text{H}_9$  (VIII);  $\text{C}_6\text{H}_{11}$  (IX);  $\text{C}_{10}\text{H}_{17}$  (X). From the butynal acetals we obtained the corresponding butyral acetals:  $\text{C}_4\text{H}_8(\text{OR})_2$ , where  $\text{R} = \text{C}_4\text{H}_9$  (XI)  $\text{C}_6\text{H}_{11}$  (XII). The ethynylvinyl ethers brominate readily. Thus, the ether molecule absorbed two moles of bromine when ethynylvinyl butyl ether was saturated with bromine. The first mole of bromine probably adds to the double bond with simultaneous isomerization. The second mole of bromine adds to the triple bond with the formation of 1-butoxy-1,2,3,4-tetrabromo-2-butene (XIII):



In support of such a structure for the tetrabromo ether is the fact that in aqueous medium it can be quantitatively titrated with 0.1 N NaOH, which indicates that it contains an  $\alpha$ -Br atom, while from the hydrolyzate we isolated tribromocrotonaldehyde (Equation (5))



The enumerated reactions testify to the substantial reactivity shown by ethynylvinyl ethers in ionic transformations, manifesting some of the properties of the double bond contained in them. Using diacetylene as a base we synthesized 16 compounds, of which 10 are new.

## EXPERIMENTAL

**Preparation of Diacetylene.\*** 2-Butyn-1,4-diol was chlorinated with thionyl chloride at  $-15^\circ$  to  $+10^\circ$  for 12 hours, and then heated to  $60^\circ$  until all of the  $\text{SO}_2$  had been removed from the reaction mixture. The dichlorobutyn was vacuum-distilled at a pot temperature not exceeding  $110^\circ$ . The yield was 70% of theory. A mixture of 24 g of the dichlorobutyn, 3 g of ethanolamine and 50 g of ethyl alcohol was heated with stirring in a nitrogen stream to  $70-75^\circ$ , and then 80 ml of 40% NaOH was added dropwise. The diacetylene was passed through concentrated NaOH solution and dry  $\text{CaCl}_2$ , and then was condensed in a coil receiver at  $-70^\circ$ . The yield of diacetylene was 6.35 g (50% of theory).

**Reaction of Diacetylene With Butanol, Cyclohexanol and  $\beta$ -Decalol.** A 2% solution of potassium hydroxide in alcohol was placed in a cylindrical reaction vessel, fitted with stirrer and reflux condenser. After flushing the system with dry nitrogen a stream of diacetylene was passed into the reaction vessel, heated in a vaseline bath. On conclusion of reaction the mixture was washed with water, dried over potash, and vacuum-distilled. The isolated products were colorless liquids; they give a positive test for the triple bond. The characteristics of the isolated compounds are listed in Table 1.

**Reaction of Butyl Ethynylvinyl Ether (I) With Butyl Alcohol [3] in Acid Medium.** To a stirred mixture of 4.1 g of butyl ethynylvinyl ether (I) and 4.6 g of butanol was added 1 drop of conc.  $\text{H}_2\text{SO}_4$ . After neutralization of the catalyst the mixture was vacuum-distilled. We collected 3.5 g of a fraction with b.p.  $92-96^\circ$  (6 mm), which after redistillation had the constants of the dibutyl acetal of 2-buten-4-ol (IV): b.p.  $103-104^\circ/9$  mm;  $n_D^{20} = 1.4400$ ;  $d_4^{20} = 0.8764$  (Table 2). Yield 55% of theory.

\* By the Herberts method, which was improved upon in our laboratory with the assistance of E. V. Dubrova.



TABLE 1  
Preparation Conditions and Characterization of the Isolated Ethers and Acetals

Compound formula	Mole ratio alcohol/ diacetyl- ene	Yield % of theory	Reaction tempera- ture	B.p. °C/mm	$n_D^{20}$	$d_4^{20}$	MR		M	Found, %		Calculated %		B.p. °C/mm
							found	calc.		C	H	C	H	
$\text{CH}_3\text{C}\equiv\text{C}-\text{CH}-\text{CH}-\text{OC}_2\text{H}_5$	(I) 3:1	60.0*	100-110	60-60.5/11 144° at p.	1.4702	0.8662	40.02	38.25	122.0	77.52	9.71	77.36	9.55	176-178 (°)
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$	(IV) 4:1	25.6**	120-125	105/11	1.4308	0.8758	59.71	59.97	198.0	72.53	11.04	72.70	11.17	78-85/3 (°)
$\text{CH}_3\text{C}\equiv\text{C}-\text{CH}-\text{CH}-\text{OC}_2\text{H}_5$	(II) 5:1	40.0*	95-98	85.8/8.5	1.5035	0.9463	46.96	45.29	146.3	73.61	9.34	79.96	9.39	100-105 (°)
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$	(V) 5:1	30.5**	130-137	125.5-126/3	1.4890	0.9852	73.36	74.04	248.0	76.46	10.28	76.76	10.47	165-167 (°)
$\text{CH}_3\text{C}\equiv\text{C}-\text{CH}-\text{CH}-\text{OC}_2\text{H}_5$	(III) 3:1	60.0*	90-95	130.5/4.5	1.5298	0.9945	63.13	61.56	199.0	82.19	9.59	82.28	9.86	—

\* In addition, the butynal acetal was isolated.

\*\* In addition, the ethynylvinyl ether was isolated.

TABLE 2  
Hydrogenation of Ethynylvinyl Ethers and Butynal Acetals

No. of starting compound	Obtained compound	Yield % of theory	B.p. °C/mm	$n_D^{20}$	MR		Found, %		Calc. %		From the literature		Refer- ence
					found	calc.	C	H	C	H	B.p. °C	$n_D^{20}$	
I	$\text{C}_6\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	(VIII) 80.0	81-82/51	1.4602 (15°)	40.51	40.77	—	—	—	—	141.9/750 mm	1.4610 (15°)	(14)
IV	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}(\text{OC}_2\text{H}_5)_2$	(XI) 75.0	138-9	1.4153	59.99	60.90	70.93 71.06	12.90	71.22	12.85	—	1.4211 (17.5°)	(15)
II	$\text{C}_6\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	(IX) 89.0	193-41 at p.	1.4380	47.41	47.82	—	—	—	—	193.5 194.5 at p.	1.4385	(16)
V	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}(\text{OC}_2\text{H}_5)_2$	(XII) 78.8	120-113.5	1.4665	75.04	74.97	79.72	11.90	79.55	12.45	—	—	—
III	$\text{C}_6\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	(X) 82.0	133-134.5/10	1.4772	64.19	64.09	79.91	11.90	—	—	—	—	—
III	$\text{CH}_3-\text{CH}-\text{CH}-\text{CH}-\text{OC}_2\text{H}_5$	(VII) 80.0	110 4/2	1.5040	63.16	63.07	81.29 81.50	10.81 10.71	81.48	10.75	—	—	—

Hydrolysis of  $\beta$ -Decalyl Ethynylvinyl Ether (III) in Acid Medium. a) A mixture of 5 g of (III) and 25 ml of 10%  $H_2SO_4$  was heated to 80° for 1 hour. Distillation of the oil layer gave 2.8 g (85% of theory) of  $\beta$ -decalol with b.p. 142-143°/33 mm,  $n_D^{20} = 1.5010$ . From the water layer we isolated the semicarbazone of 1-butyne-4-al with m.p. 120°. The literature m.p. is 122° [3].

In addition, we isolated 0.22 g of triacetylbenzene with m.p. 164° (in the literature, 165° [3], the formation of which is explained by the accompanying hydration and trimerization of the aldehyde.

Hydrogenation of Ethynylvinyl Ethers and Butynal Acetals. The hydrogenation was run at room temperature in methanol solution: exhaustive hydrogenation over Pt, and partial hydrogenation over Pd. The experimental results are shown in Table 2.

Bromination of Ethynylvinyl Butyl Ether (I). A solution of 12.6 of bromine in 5 ml of  $CCl_4$  was added in drops to a solution of 3.65 g of (I) in 3 ml of  $CCl_4$  at -10°. The reaction mixture was stirred at room temperature for 2 hours. We obtained 11.3 g of crystalline butyl 1,2,3,4-tetrabromo-2-butene ether (XIII), which after recrystallization from petroleum ether had m.p. 59-60°. The yield was 88.2% of theory.

Hydrolysis of Butyl 1,2,3,4-Tetrabromo-2-butene Ether (XIII). a) A mixture of 0.1476 g of (XIII) and 25 ml of water was shaken in a flask at room temperature for 1 hour. To titrate the hydrolyzate required 2.89 ml of 0.01 NaOH, which corresponds to 99.8% of titrable H [10]. b) A mixture of 5.4 g of the tetrabromo ether (XIII) and 20 ml of water was boiled for 1 hour. The oil layer was dried over sodium sulfate and then vacuum-distilled. We collected 3.3 g (87.4 %) of a fraction with b.p. 128-135°/2 mm, which after redistillation proved to be 1,2,3-tribromocrotonaldehyde (XIV). B.p. 137-138°/3 mm;  $n_D^{20} = 1.6540$ ;  $d_4^{20} = 2.6150$ ,  $M_D = 43.00$ , calc.  $C_4H_3OBr_3/MR = 43.42$

Found %: C 15.45; 15.54; H 1.04; 1.09; Br 78.59; 78.86  $C_4H_3OBr_3$ . Calculated %: C 15.66; H 0.99 Br 78.13

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